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COMPENDIUM ON LIMES IN HYDROMETALLURGY AND FLOTATION

This report presents the results of work done under a cooperative agreement between the U. S. Bureau of Mines and the Missouri School of Mines and Metallurgy, Rolla, Mo.

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R. G. O'MEARA, ALEXANDER M. GOW, AND W. T. SCHRENK

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DEPARTMENT OF COMMERCE - BUREAU OF MINES

COMPENDIUM ON LIMES IN HYDROMETALLURGY AND FLOTATION[1]

- By -

R. G. O'Meara[2], Alexander M. Gow[3], and W. T. Schrenk[4]

INTRODUCTION

Lime is used extensively in the various industries. The National Lime Association[5] in an excellent and recent bulletin lists 23 important industries in which lime plays a vital role; and it thereby justifies the statement that "Lime is one of the most versatile and widely used reagents in the chemical and industrial world." There is, however, one application of this "universal" reagent which has not been mentioned. It is the use of lime in the flotation of ores. An appreciable percentage of the lime production is consumed by ore-dressing plants.

The uses of lime throughout all the industries are more or less related, but "lime" is a broad term; the varieties of lime are more numerous than the limestones from which it is made, and its use involves a complicated technique. The interrelated application and growing importance of lime in flotation warrant this additional publication on the various "limes," with emphasis on those uses related to the function of lime in flotation.

Lime in water treatment, cyaniding, and amalgamating will be mentioned, after which its use in flotation will be taken up.

This compendium was prepared by the Mississippi Valley Experiment Station of the United States Bureau of Mines and the Missouri School of Mines and Metallurgy, Rolla, Mo.

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1 - The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from the U. S. Bureau of Mines Information Circular 6423."

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5 - National Lime Association, Lime: Its Uses and Value in the Industrial and Chemical Processes; Washington, D. C., 1930, 88 pp.

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Lime was one of the first chemical substances used by mankind. Knibbs[6] gives an interesting historical sketch of lime, stating that it is as old as the use of fire, that it was used as an offensive weapon in war by throwing it into the faces of the enemy, and that magnesia was not clearly distinguished from lime until the eighteenth century:

> Lime was one of the first chemical substances to be used by mankind, and lime-burning is one of the oldest chemical industries. The process of calcining limestone is probably nearly as old as the use of fire, because in any limestone country the effect of lighting a fire on the stone would be to produce lime, but the intelligent application of the process must have come much later . . . . .
>
> According to Quietmeyer, lime, together with plaster of Paris, was used in Egypt about B. C. 2600, and by Soloman in Jerusalem circa 950 B. C., and it is probable that its use began at a much earlier age . . . . . Xenophon (circa B. C. 350) records the wrecking near Marseilles of a ship carrying a cargo of linen and the lime required for its bleaching, but Cato, in B. C. 184, appears to have been the first to mention kilns for burning it. Dioscorides and Pliny (circa A. D. 75) both describe the production, slaking, and uses of lime . . . . . Vitruvius, at the beginning of the Christian era, dealt at length with the use of lime for building purposes. Lime is mentioned in the Bible . . . . . .
>
> Little is known regarding the condition of the lime industry in medieval times, but a knowledge of its properties and its use for building purposes is reflected in the writings of the day . . . . .
>
> Quicklime would appear to have been used in the Middle Ages for offensive purposes in war, and the English hurled it in their enemies' faces at a naval battle just after the death of John in 1217 . . . . . It was used by alchemists for causticizing the alkali metal carbonates in wood ashes and for other purposes, but it was so familiar a material that they seldom thought it worth mentioning, and no attempt seems to have been made to explain the nature of the process of calcination until the phlogistic period.
>
> The elucidation of the nature of the calcination process is due largely to Joseph Black, who showed that it consisted in the expulsion of 'fixed air.' . . . . . .
>
> Magnesia was not clearly distinguished from lime until the 18th century when Black showed that the former gave a soluble sulphate. It therefore has no individual early history. Magnesia alba appears to have come into commerce from Rome about A. D. 1700. The calcination of magnesium carbonate, like that of calcium carbonate, was explained by Black and Lavoisier.

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6 - Knibbs, N. V. S., Lime and Magnesia: Ernest Benn, Ltd., London, 1924, 300 pp.

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Limestone, from which lime is made, is one of the important substances in the lithosphere. That it is widely distributed upon the earth is shown by Clarke.[7] He shows that the average limestone is only about 75 per cent pure and states as follows:

> . . . . . Broadly, then, we may estimate that the lithosphere, within the limits assumed in this memoir, contains 95 per cent of igneous rock and 5 per cent of sedimentaries. If we assign 4.0 per cent to the shales, 0.75 per cent to the sandstones, and 0.25 per cent to the limestones we shall come as near the truth as is possible with the present data . . . . . .

Whether or not the figures are correct is of no importance to us other than it does show that the distribution is widespread. Nor has the United States been slighted in the matter of geologic distribution of limestone. The statistics published by the Department of Commerce, Bureau of Mines, for 1928[8] show that 41 of the 48 States have reported plants in operation for the burning of lime. In 1928 the four largest producing States were Ohio, Pennsylvania, Missouri, and West Virginia, in the order named. The total number of plants in operation in 1928 was 411. Keen competition existed among the producers and there was a tendency to overproduction and lower prices. If lime is the most plentiful alkali, it is also the cheapest. The average value, at the plants, of lime sold decreased from $8.75 a ton in 1927 to $8.18 a ton in 1928. In 1929 the average price for hydrated lime was $8.24 per ton. The average value for building lime was 85 cents less than in 1927, for chemical lime was 24 cents less, and for agricultural lime was 8 cents less. The production of lime in the United States from 1919 to 1929, inclusive, is given in Table 1, taken from Mineral Resources of the United States, 1928.[9]

The statistics given in Mineral Resources do not include a considerable amount of lime that is not a commercial product, but is burned for direct use in manufacturing, from stone either quarried or purchased by the manufacturer. This stone is reported to the Bureau as raw limestone and is included in the statistics on stone. It is used mainly by alkali works, sugar refineries, and smelters.

As mentioned in historical sketches on lime, the first recorded use was in mortar and plaster. The field has since extended so that lime is a necessity in many industries. Holmes[10] mentions the extensive uses of lime:

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7 – Clarke, Frank Wigglesworth, The Data of Geochemistry: U. S. Geol. Survey, Bull. 770, 1924, p. 34.

8 – Coons, A. T., Lime in 1928: Mineral Resources of the United States, 1928 - Part II, 1929, pp. 175-186.

9 – Coons, A. T., Work cited.

10 – Holmes, M. E., An Outline of the Uses of Lime: Chem. and Met. Eng., vol. 26, Feb. 15, 1922, pp. 294-300.

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Table 1. - Lime sold by producers in the United States, 1919-1929

Year	Hydrated lime			Total lime		
	Number of plants in operation	Short tons	Value[1]	Number of plants in operation	Short tons	Value[1]
1919	93	779,408	$ 7,061,146	539	3,330,347	$ 29,448,553
1920	98	853,116	9,287,562	515	3,570,141	37,543,840
1921	105	792,970	7,421,637	520	2,532,153	24,895,370
1922	114	1,106,063	9,868,980	530	3,639,617	33,255,039
1923	121	1,225,928	12,229,598	467	4,076,243	39,993,652
1924	120	1,316,664	13,199,846	450	4,072,000	39,596,423
1925	134	1,560,848	15,287,461	450	4,580,823	42,609,141
1926	147	1,606,811	15,182,460	435	4,560,398	41,566,452
1927	157	1,596,906	14,581,695	417	4,414,932	38,638,413
1928	164	1,612,818	13,540,215	411	4,458,412	36,449,635
1929[2]		1,550,771	12,771,525	381	4,269,768	33,478,848

1 - The value given represents the value of bulk lime f. o. b. point of shipment and does not include cost of barrel or package.

2 - Advance figures from press release of Department of Commerce on "Sales of Lime in 1929;" Sept. 16, 1930.

The use of lime in mortar and plaster was, in past ages, its only important use. Coincident with our modern industrial development along technical lines, the lime industry has expanded enormously in the number of its technical uses and thereby has offered a fertile field for the activities of the investigator and writer . . . . . .

In the present article the author has approached the subject primarily from the point of view of a systematic arrangement in outline form of the uses of lime, grouping the various uses under headings indicating functions performed by lime. In order to show the unusually large number of functions that lime can perform, we have included not only the well-known uses that represent large tonnages but all the uses of which we have authentic records.

. . . . . .

In industrial technology it is convenient to divide the uses of lime into three major groups - viz., construction uses, agricultural uses, and chemical uses. The construction uses include those involved in building operations, the agricultural uses are limited to the uses on the farm, and the chemical uses include the very large number involved in manufacturing and technical processes. Although the allocation of certain uses is somewhat arbitrary, yet it seems to divide the field in accordance with the duties of the engineer, agronomist, and chemist.

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Holmes gives in his article a table of the relative importance of the various uses of lime, compiled from data for 1921 given by the United States Geological Survey. The latest available figures (1928) taken from Coons[11] on lime are given in Table 2 and rearranged to have the same form as the table shown by Holmes.

The table shows that in 1928, 504,248 tons of lime was used for metallurgical work. The consumption of lime in flotation for the same period was about one-fifth of this amount. From this the conclusion is drawn that about 2.5 per cent of all the lime consumed is used in flotation.

CLASSIFICATION OF LIMES

Lime in the true sense of the word denotes calcium oxide, but within the industry, usage and the varied chemical composition of limestone, from which the lime is obtained by calcination, have extended the meaning so that it also connotes a large variety of products varying in composition with regard to the CaO--MgO ratio. A classification is given in Table 3 which is a modification of one by Knibbs.[12] This classification serves to remind the flotation operators that due attention should be given to the composition of the lime purchased.

Ladoo[13] discusses the divergence of commercial limes from the true chemical significance of the term lime as follows:

> . . . . . By proper chemical nomenclature lime is calcium oxide (CaO), but, commercially, lime is understood to mean the product of complete calcination of a limestone, which may vary from pure calcium carbonate ($CaCO_3$) to pure dolomite ($CaCO_3 . MgCO_3$). Thus, commercial lime may contain as high as 45 per cent of magnesium oxide (MgO) as well as such impurities as silica, iron oxide, and alumina.

Another author[14] discusses the variation in limes in the following manner:

> The term 'limestone' is used to describe a class of rocks varying in composition from pure calcium carbonate to a mixture of 54.35 per cent calcium carbonate with 45.65 per cent magnesium carbonate. (According to definition by National Lime Association.) Any gradation between these limits may be found, and all limestones contain more or less impurities. In the same way lime may vary from pure calcium oxide to a mixture of calcium and magnesium oxides in the corresponding proportions.

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11 - Coons, A. T., Work cited.
12 - Knibbs, N. V. S., Work cited.
13 - Ladoo, Raymond B., Non-metallic Minerals; McGraw-Hill Book Co., New York, 1925, p. 310.
14 - Porter, J. M., Manufacture of Lime: Bureau of Standards Cir. 337, 1927, p. 4.

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Table 2. - Relative importance of the various uses of lime

Uses	Percentage of total		Short tons	
	1927	1928	1927	1928
BUILDING	48.7	44.6	3,148,840	1,986,465
CHEMICAL:				
Sugar refineries	.4	.5	16,086	22,678
Tanneries	1.4	1.4	63,666	64,464
Glass works	1.8	1.7	78,994	76,161
Refractory lime (dead-burned dolomite)	8.5	10.1	374,415	448,761
Metallurgy	9.2	11.3	406,063	504,248
Paper mills	9.7	9.6	429,606	429,334
OTHER USES:	13.0	13.3		
Alcohol manufacturing and dehydration			2,199	2,302
Alkali works (ammonia, soda, potash)			19,610	6,675
Bleaching powder			5,723	14,970
Bleach liquid			10,308	18,954
Calcium acetate			9,618	1,643
Calcium carbide			27,037	32,596
Coke and gas manufacturing (gas purification and plant by-products)			29,988	31,011
Creameries and dairies			(1)	- -
Disinfectants (chloride of lime, etc.)			(1)	- -
Flour mills			(1)	- -
Glue			7,864	8,467
Insecticides (spraying material)			22,154	19,269
Oil and fat manufacturing			3,899	9,119
Oil refining			7,101	(1)
Paint (kalsomine, whitewash, varnish, etc.)			5,050	5,017
Rubber			4,192	3,361
Salt refining			1,210	2,423
Sand-lime and slag brick			43,064	47,527
Sanitation (sewage, garbage purification, etc.)			2,416	2,857
Silica brick			15,638	15,735
Soap			25,487	33,759
Textiles			1,128	1,460
Water purification			124,212	145,757
Wood distillation			11,682	3,899
Undistributed(2)			42,973	53,198
Unspecified			151,816	132,392
Agricultural	7.3	7.5	322,893	333,910
Total	100.0	100.0	4,414,932	4,458,412
Hydrated lime (included in above totals)	36.2	36.2	1,596,906	1,612,818

(1) Included in "undistributed."

(2) Lime used in acid neutralization and drying, acetic acid, asphalt and fertilizer filler, bichromate refining, buffing compounds, calcium phosphate, cellulose, corn products, creameries and dairies, cyanide manufacture disinfectants (chloride of lime, etc.), dyes, flour mills, food products, gelatin (edible), magnesia oil refining, oxygen, purification, retarder, and stock food.

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Table 3. - Classification of limes

Oxide	Hydroxide	Composition of carbonate		
		$CaCO_3$, per cent	$MgCO_3$, per cent	Other compounds, per cent
Calcium oxide (pure)	Calcium hydroxide (pure)	100	-	-
Lime High-calcium lime Quicklime Fat lime Caustic lime Shell lime	Hydrate of lime Hydrated lime Slaked lime High-calcium hydrated lime Caustic lime	90 to 100	0 to 10	0 to 10
Siliceous lime Argillaceous lime Hydraulic lime Lean lime	Hydrated siliceous lime, etc.	50 to 90	0 to 10	10 to 50
Magnesian lime Dolomitic lime	Magnesian hydrated lime; Hydrated magnesian lime, etc.	60 to 90	10 to 40	0 to 10
Dolomitic lime Dead-burned lime	Hydrated dolomitic lime	50 to 60	40 to 50	0 to 10
Dolomitic magnesia or dead-burned dolomitic magnesia	-	20 to 50	50 to 80	0 to 10
Magnesia Dead-burned magnesia	-	0 to 20	80 to 100	0 to 10

Eckels[15] gives the following classification of commercial limes:

Group A. High calcium limes: Limes containing less than 5 per cent of magnesia. The limes of this group differ among themselves according to the amount of silica, alumina, iron, etc., contained. A lime carrying less than 5 per cent of such impurities is a 'fat' or 'rich' lime, as distinguished from the more impure 'lean' or 'poor' limes.

15 - Eckels, Edwin C., Cements, Limes and Plasters: New York, 1928, pp. 98-9.

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Group B. Magnesian limes: Limes containing over 5 per cent (usually 30 per cent or over) of magnesia. These limes are all slower slaking and cooler than the high-calcium limes of the preceding group, and they appear to make a stronger mortar. They are, however, less plastic or 'smooth', and in consequence are disliked by workmen. As commercially produced, they usually carry over 30 per cent magnesia.

Holmes and Fink[16] give a slightly different classification:

. . . . . By the term commercial lime, we refer to the three and one-half million tons of product made yearly in this country by calcining limestone and which is placed on the market without any further processes of chemical purification. That this material may be quite different from corresponding c. p. chemicals is evident from the following definitions as adopted by the American Society for Testing Materials:

'Quicklime is a calcined material, the major part of which is calcium oxide or calcium oxide in natural association with a lesser amount of magnesium oxide capable of slaking with water.

'Hydrated lime is a dry powder made by treating quicklime with enough water to satisfy its chemical affinity under the condition of its hydration. It consists essentially of calcium hydroxide or a mixture of calcium hydroxide and magnesium oxide and magnesium hydroxide.'

Commercial limes are further classified by the A. S. T. M. on the basis of alkaline-earth oxide ratio as calcium and magnesium limes. In common practice calcium lime is one containing 85 per cent or more total CaO and magnesium lime is one containing more than 10 per cent MgO. In case the CaO content is very high, it may be called high calcium lime and in case the magnesium oxide is considerably more than 10 per cent it may be called high-magnesium lime.

Ladoo[17] gives practically the same classification with more information on the subject of impurities.

Lime is sold in two forms: (1) Quicklime (CaO), and (2) hydrated lime $Ca(OH)_2$. Hydrated lime is formed from quicklime by adding the requisite amount of water. When quicklime is exposed to the air for some time, it gradually absorbs carbon dioxide (CO_2) from the air and 'air-slakes,' or reverts to its original form of calcium carbonate ($CaCO_3$).

Commercial limes are classified according to their relative content of CaO and MgO as follows:

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16 - Holmes, M. E., and Fink, G.J., Fundamental Physical and Chemical Properties of Commercial Lime; I - Available Lime Content: Chem. and Met. Eng., vol. 27, Aug. 23, 1922, p. 347.

17 - Ladoo, R. B., Work cited.

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High-calcium lime: Not less than 90 per cent CaO.

Calcium lime: Not less than 85 per cent nor more than 90 per cent CaO.

Magnesian lime: Not less than 10 per cent nor more than 25 per cent MgO.

High magnesian lime: Not less than 25 per cent MgO.

Total impurities (exclusive of carbon dioxide) should not be over 5 per cent in selected lime or 7.5 per cent in run-of-kiln lime.

In the following[18], the leanness of limes is attributed to argillaceous components instead of magnesium oxides as is the general practice:

> Usually the limit of MgO for 'fat limes' is taken as 5 to 9 per cent. However, in Palermo and Lombardy they use fat limes obtained from dolomitic limestones which contain as high as 40 per cent MgO. These limes are free from or contain very little SiO_2, clay, etc., while these impurities are present in considerable quantities in 'lean' limes. Hence the 'leanness' of limes is due, not to MgO, but to SiO_2 or other argillaceous components.

Thus, as was said before, "lime" is a broad term. Rarely is commercial lime free from impurities, however, are not necessarily harmful; but designation should be made as to the type of lime under consideration. In general, limes may be classified as "high-calcium" or "high-magnesium," or as "fat" or "lean," depending on the chemical composition of the stone from which they were produced. Such classification is important since the different varieties have different properties. In addition to the composition, the manner of calcining also determines the character of the product.

MANUFACTURE OF LIME

The manufacture or burning of lime may be defined as the process of converting limestone into lime through the agency of heat. The impurities may or may not be removed. It is apparent, therefore, that the burning of lime is concerned merely with the removal of carbon dioxide from the stone. When the stone is heated to a sufficiently high temperature and kept there for a sufficiently long time, the carbonates are dissociated and the carbon dioxide is driven off as a gas.

In the manufacture of lime, limestone is quarried, broken into convenient sizes, and calcined in a kiln. Most of the quicklime produced in this country is made in shaft kilns in which the selected limestone is subjected to a temperature above that of the decomposition of calcium carbonate (900° C.) for a sufficient time to drive off the carbon dioxide. Commonly, kiln temperatures range from 1,200 to 1,400° C. The quality of limestone suitable for

18 - Occhipinti, Francesco, Influence of Magnesia Upon the Character of Aerated Limes: Giorn. Chim. ind. Applicata, vol. 6, 1923, pp. 17-20.

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burning may vary both chemically and physically within rather wide limits. Porter[19] says:

> . . . . . It must be remembered that on account of the loss of about half the weight of the stone as carbon dioxide during the burning the proportion of every other constituent of the stone will be nearly doubled in the lime . . . . . The amount of impurities (silica and oxides of iron and aluminum) permissible in a finishing lime (quicklime or hydrate) is very small, certainly not over 5 per cent (2-1/2 per cent in the stone).

The best burning of lime is obtained by using the minimum amount of heat. Porter[20] states as follows:

> There are three factors essential to the purpose of lime burning: (1) The stone must be heated to the temperature of dissociation of the carbonates; (2) the temperature must be maintained for a certain length of time; (3) the carbon dioxide evolved must be removed.
>
> Many experiments have been made to determine the temperature of dissociation of calcium carbonate. The best and most recent work done on this subject has been by Johnson and Mitchell. Both of these investigators found the dissociation temperature to be 898° C. The corresponding temperature for magnesium carbonate has not been determined as accurately and the results are not at all concordance, but the value 756° C. obtained by Mitchell in 1923 is probably quite correct. These figures are for a pressure of one atmosphere of carbon dioxide, a condition hardly ever met with in practice. The dissociation temperature of stones containing magnesium carbonate depends upon the manner of combination of the two carbonates. Some investigators have found the two materials to behave as separate compounds, dissociating at their respective temperatures. On the other hand, others have found the behavior to indicate the presence of a double salt, with the dissociation temperature lying between that of calcium carbonate and magnesium carbonate. Recent work conducted at this bureau indicated the latter condition to be true.
>
> After the dissociation temperature has been reached it must be maintained for some time in order to transfer the required amount of heat to the stone . . . . . .
>
> The physical properties of the stone undoubtedly have some influence on the amount of heat required and the time in which this heat can be transferred to any given temperature. Thus, it will take longer to burn a large piece of stone than a smaller one. A fine-grained, dense stone will conduct the heat more readily than

19 - Porter, J. M., Page 6 of work cited.
20 - Ibid., p. 8.

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one which is coarsely crystalline and porous. Practical experience seems to point to the fact that the crystals themselves require more heat to dissociate them than the more fine-grained stone. The time required to transfer a given amount of heat, roughly speaking, varies inversely with the temperature difference. Therefore, it has been found economical to use as high a temperature as possible in order to reduce the time required for burning. The upper limit of the temperature is determined by the phenomenon of 'overburning.' Overburned lime can be recognized by its yellow color and the extreme length of time it takes to slake, together with the fact that it is appreciably heavier than the white, properly burned lime. These properties are probably caused by the chemical combination of the lime with impurities (especially with silica and silicates) contained in it and the reduction in the percentage of pore space in the quick-lime. Lime may be overburned by being heated for too long a time as well as at too high a temperature. In general, it is better to underburn than to overburn the lime, for the unburned stone may be put back into the kiln while the overburned lime is useless. Moreover, the properties of overburning seem to assert themselves gradually, so that the best lime is obtained by using a minimum amount of heat.

Knibbs[21] attributes the character of the quicklime to several factors:

The properties of calcium oxide depend on the method of its formation, the temperature to which it has been exposed and the duration of the heating . . . . . .

It also depends upon the physical properties of the carbonate. According to Kohlschutter and Feitknecht the primary particles of burnt lime are crystalline, preserving more or less the structure of the original substance, but on continued heating they aggregate to form secondary particles.

Knibbs[22] emphasizes the necessity of proper calcining temperature when he says:

The chemical properties of magnesium oxide depend, even more than those of calcium oxide, on the temperature to which it has been heated and the duration of the heating.

. . . . . The oxide prepared by heating the native carbonate . . . . . to redness when mixed with a limited amount of water sets hard, but this property of hard setting is not shared by all oxide made at low temperature. Some low temperature oxide absorbs water, like calcium oxide, without setting. If the oxide is heated to a high temperature it loses the property of absorbing water, especially if it contains a trace of iron oxide, when artificial periclase is formed . . . . . Even the high temperature product, however, combines slowly with water.

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21 - Knibbs, N. V. S., Page 48 of work cited.
22 - Knibbs, N. V. S., Page 74 of work cited.

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Knibbs[23] warns against the overburning of magnesium limes since:

> Magnesian limes and magnesite are similarly subject to overheating, and the temperature at which they were dead-burned is much lower than that of pure lime . . . . . .

Since lime, in most chemical and all flotation uses, functions in an aqueous solution, the reactions in water are far more important to the ore dressing engineer than the fire reactions. The calcining should, therefore, be of such a nature as to produce a quicklime which is favorable to hydration.

The rate of hydration is determined by the physical and chemical properties of the quicklime which is being used. With subsequent hydration in mind, Knibbs[24] gives an explanation of the physical conditions of quicklime recently advanced, but the matter has never been fully investigated. The physical and chemical properties are closely related, for the physical modifications are due to chemical impurities in many cases. To quote Knibbs:

> In the operation of lime burning it frequently happens that lumps of lime are produced which when wetted hydrate only very slowly. Such lime is said to be over-burnt or dead burnt. It is usually easily distinquishable from good active lime by its appearance and its weight, white lime generally assuming a yellow tinge and becoming appreciably heavier when overburnt. The difference in the rate of hydration may be enormous. A good piece of lime on wetting may become hot and start to fall to a powder in a few seconds, whilst an over-burnt piece of lime may remain apparently unchanged for hours or even days. The term used for this slow-slaking lime implies the fact that its condition is due to overheating or to its remaining for too long a period at the high burning temperature, but an explanation of the change in the lime which so alters the rate of hydration has been suggested only comparatively recently, and the phenomena has never been fully investigated . . . . . .
>
> Since compact crystalline carbonate dissociates and the carbon dioxide escapes without any breaking up of the solid, which retains exactly the shape and size of the original carbonate, it is clear that the resulting oxide must be porous and of a very fine-grained structure . . . . . In spite of its high melting point, lime softens at a comparatively low temperature, and it is clear that the exceedingly fine-grained structure which must be formed when the carbonate first parts with its carbon dioxide may rapidly change on continued exposure to heat. The change will obviously be in the direction of reducing the exposed surface of the oxide, that is to say, the size of the individual cells or pores in the lime structure will increase whilst the area of the enclosing walls will be reduced. This may continue for some time without any reduction in the total volume of the lump, but finally we should expect the cells to contract and the size of the whole lump to diminish, the percentage of pore space

23 - Knibbs, N. V. S., Page 101 of work cited.
24 - Knibbs, N. V. S., Work cited, p. 99 et. seq.

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being reduced. There is good reason to believe that these changes actually do take place under the influence of heat.

It must also be remembered that just as the solubility of a solid is affected by its surface conditions, so its chemical activity is similarly influenced, and an exceedingly fine-grained structure, which resembles a very fine powder, is more reactive than a coarse structure or a smooth surface.

In commercial lime we have also to take into account the impurities which are always present, and which reduce the activity of the oxide in two ways. In the first place, they are diluents. Silica, for example, combines with calcium oxide to form the compound 3 CaO . SiO_2 and in addition to the three molecules which are thus rendered entirely inactive the calcium silicate acts as a diluent to the oxide. Moreover, at high temperatures either more basis compounds or solid solutions of the silicate with calcium oxide are formed, and the additional oxide so combined or associated with the silica is rendered entirely or partially inactive. Alumina and iron oxide act in the same way as silica. In the second place, these impurities increase the tendency towards the reduction of surface by reducing the temperature at which softening, and therefore contracting, takes place. The combination of these two effects accounts for the very considerable influence which the amount and type of the impurities exert on the relation between activity and burning temperature.

HYDRATION

Hydrated lime, the dry hydrate, is a produce of comparatively recent origin. It is lime in which the combination with water has already taken place. Holmes and Fink[25] say:

> Hydrated lime is now made by mechanical processes which vary somewhat, but all involve the thorough mixing of quicklime with the predetermined quantity of water required for complete hydration and maintenance of the most favorable conditions for hydration . . . . .

Until recently most of the lime used in the building industry and some of the lime consumed in the chemical industry was hydrated by hand. However, a good mechanical hydrator does the work better. Mechanical hydrators are of two types: Those that hydrate to a milk of lime and those in which the hydration is to a dry powder.

Lime sometimes burns when slaking. This is discussed by Porter[26], who says:

> The actual slaking of the lime takes place in an apparatus called the hydrator. Theoretically, the only function it has to perform is to mix the lime and water thoroughly and quickly, to prevent burning

25 – Holmes, M. E., and Fink, G. J., Page 347 of work cited.
26 – Porter, J. M., Pages 68 and 69 of work cited.

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> the lime by local overheating. Just what happens when lime 'burns' during slaking is not well understood. If a lump of lime is given enough water to start hydration but not enough to complete the process, the unslaked portion will 'burn', and become practically useless. This phenomenon is probably due to some change in the physical condition of the lime caused by concentrating the heat. It is, therefore, absolutely necessary that sufficient water be added and that it shall be mixed with the lime very thoroughly and quickly . . . . . .

Whatever the system of hydration, the material discharged from the hydrator is much the same. Knibbs[27] states:

> Whatever the system of hydration, the material discharged from the hydrator is a mixture of fine hydrate and lumps of unhydrated lime, lumpy hydrate, impurities, unburnt stone, etc. Some manufacturers grind the lime very finely before hydration, but this practice is not to be recommended because it prevents the separation of good fine hydrate from impurities, etc., which should be the first step after the process of actual hydration . . . . .
>
> The fine hydrate is separated from the coarse material by means of either screens or air separators.

A booklet by the American Steel and Wire Co.[28] in discussing the slaking of lime recommends the use of hot water and not more than 4 pounds of water to 1 pound of lime. It drops the caution that the lime so slaked does not wholly loose its granular nature. It says:

> When quick lime is treated with water, heat is given off and the lime is reduced to paste or mud of lime. If core is present, lumps of it will be found unslaked. Not more than four pounds of water should be added to one of lime to slake it. If convenient, hot water gives better and quicker results than very cold water. In fact, very cold water should be used very carefully in slaking lime. If too much be used at one time, the lime will not slake properly. On the contrary, care must also be used in slaking lime with warm water, lest the lime get too hot and burn. When it gets too hot, more water should be added and the lime stirred with a mortarman's hoe. In case mechanical stirring devices are provided, the lime can be stirred mechanically and this is much better than using manual labor. Any soft, mushy lumps must be broken up to allow the water to get to the center of them. When the lime has ceased to bubble and absorb water, it has passed the danger stage and may be left till required. It will continue to undergo more perfect slaking if left to lie as a thick mud for a number of hours.
>
> When it has been slaked it has then become a hydrated lime, and is in much the same condition that a dry hydrated lime would be if mixed into a thick mud with warm water. There is this exception: a quick lime slaked as above does not wholly lose its granular character.

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27 - Knibbs, N. V. S., Pages 193 and 194 of work cited.

28 - Manual of American Steel and Wire Co.'s System of Water Purification; January, 1916, reprinted August, 1926; Chicago, Illinois, p. 48.

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Lead or brass must not come in contact with lime. The same booklet[29] says:

> Lime will quickly attack lead and dissolve it. Brass offers a better resistance, but is rather quickly destroyed, so it is not advisable to use any lead or brass in considering devices where they will come in contact with the lime solution. Wood offers an excellent resistance, and cast iron a still better one to the action of this reagent, and therefore these two materials afford us the best possibilities for construction of the stirring devices.

Knibbs[30] summarizes some of the chemistry of lime and hydrated lime:

> Calcium oxide does not dissolve in water without first being converted into hydroxide. It therefore has no solubility in water . . . .
>
> . . . . The solubility of the hydroxide has been determined many times, and there is considerable discrepancy between some of the figures given . . . .
>
> The solubility of calcium hydroxide is increased by the presence of chlorides or nitrates of the alkali metals and ammonium, the increase being due probably to both double decomposition and the formation of complex salts (e. g. 2 $NH_4Cl.Ca(OH)_2$ or $Ca(NH_3)_2Cl_2.2\ H_2O$). It is also increased by the presence of calcium chloride or nitrate, and here the effect must be due to the formation of an oxy-salt . . . .
>
> Calcium oxide, if pure, readily combines with water to form the hydroxide. Ordinary lime, made by calcining the carbonate, is porous and on moistening a lump of it the water is at once absorbed into the pores and rapidly penetrates to its heart. Combination then sets in accompanied by an increase in volume, so that the lump breaks up, sometimes with explosive violence, and eventually falls to powder . . . . . .
>
> Exposed to ordinary air calcium oxide combines with moisture and carbon dioxide, and if originally in lump form, it falls to powder (air slaked lime). Calcium oxide at ordinary temperatures and in the absence of water apparently does not combine with carbon dioxide, and in air slaking the first reaction is the formation of the hydroxide . . . . . Pure limes hydrate rapidly (complete in 10 to 50 days), and take up more water than is theoretically required for the complete conversion of the oxide to the hydroxide. Very little carbon dioxide is absorbed until hydration is complete, and the water content decreases as the hydroxide is converted into carbonate, but an excess of water is always retained, presumably absorbed on the carbonate or hydroxide. Magnesian limes absorb both water and carbon dioxide more regularly and more concurrently. Siliceous limes are variable . . . .

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29 - See footnote 28.
30 - Knibbs, N. S. V., Pages 39, 48, and 49 of work cited.

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The properties of the hydrate vary with the method of making it. The metallurgist desires a hydrate that will remain in suspension for maximum reactivity. He can control this by regulating the amount of water used for hydration. If he buys the hydrate he should learn the method of preparation. Knibbs[31] says:

> The properties of calcium hydroxide vary considerably according to the method of its preparation and the nature of the lime from which it is made. Lime hydrated in an excess of water is generally more reactive than that made by adding just sufficient water to produce dry hydroxide . . . . . .
>
> No satisfactory explanation of these facts has yet been given, and further investigation is required. It has been suggested that the hydrate formed by dry hydration is crystalline, or in some form of molecular aggregation that renders it less soluble. It is evident that there is some difference, but its exact nature remains to be elucidated. The hydroxide formed by hydrating in excess water is very slightly dispersed, and the solubility of the minute particles formed will be appreciably higher than that of the comparatively large particles of the dry hydrate, and the time taken by the former to saturate the solution will be less.
>
> Owing to its low solubility in water calcium hydroxide is generally employed in the form of 'milk of lime' when required for a reaction in an aqueous solution. Milk of lime is a syspension of the hydroxide in a saturated aqueous solution. It may be prepared in any strength, from an actual solution containing no lime in suspension to a thick slurry which will barely flow and containing about 50 per cent of hydroxide in suspension . . . . . It is evident . . . . that lime hydrated to a dry powder is in a form that settles much more rapidly than that hydrated in excess of water . . . . . Wet hydrate on drying partially loses its property of slow settling, and resembles that prepared in a dry way, but its properties depend upon the temperature at which it has been dried.
>
> Kohlschutter and Walther, and Kohlschutter and Feitknecht have shown that the rate of settling of the hydroxide is changed by hydrating the oxide in various solutions, and they measured the rate of sedimentation in a number of salt solutions of different concentrations. They conclude that there is a colloidal form of the hydroxide between the solid and the true solution . . . . . Kosmann maintains that in milk of lime there exist various hydrates up to $Ca(OH)_2 \cdot 7 H_2O$ or $H_7 Ca(OH)_9$. It is certainly highly probable that there is some loose form of combination between the dispersed hydroxide and water, but it is doubtful whether any definite chemical compound is formed. The water molecules are probably merely absorbed. The particles of hydroxide prepared in a dry way are probably relatively large and in water the degree of dispersion is much less. Consequently

31 - Knibbs, N. S. V., Pages 50-53 of work cited.

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the exposed surface is much less and the amount of water absorbed will be correspondingly lower. Such hydroxids tends to disperse on standing in contact with water . . . . . .

Magnesium limes may be expected to settle more quickly than calcium limes. This is mentioned by Holmes and Find,[32] who state:

> The characteristics of milk of a lime suspension are of considerable importance in connection with the use of lime in many chemical and industrial processes. The rate of settling or permanancy of such a suspension is of particular and direct importance in such processes as the unhairing and plumping of hides, the preparation of glue and gelatin, the defecation of sugar juices, preparation of whitewashes and lime paints, the preparation and uses of sprays and insecticides, the treatment of water supplies, sewage disposal, treatment of textiles, and saponification and clarification of fats. In other processes involving the use of lime, such as causticizing, preparation of bleach and bleaching solutions and a number of processes in other industries, this property is of indirect importance in influencing the rate of reaction, rate of settling of sludges, etc. . . . . .
>
> The data . . . . . indicate that suspensions of magnesium limes as a class settle much more rapidly than do suspensions of calcium limes. This may probably be explained by the fact that in calcining a magnesium lime the temperature required to decompose the calcium carbonate is very much above that required for the magnesium carbonate. The resulting magnesia is therefore superheated and is not so thoroughly dispersed in the slaking of the lime. The suspensions of the material would consequently be expected in general to contain a large proportion of coarse material and to settle more freely than that obtained from high-calcium lime, which may be thoroughly disintegrated and dispersed.
>
> From a consideration of the data . . . . . it can also be said that those limes, both calcium and magnesium, which as a class have a high available lime content, settle slowest. It would naturally be expected that the higher this value the greater the number of particles of the quicklime to undergo reaction during hydration . . . . .
>
> A third generalization can be made - viz., that among the calcium limes the freshly slaked materials settle more slowly than the suspensions made from mechanically hydrated limes. As pointed out above, the conditions obtaining in the mechanical hydration are such as to favor high temperatures, which would tend to induce certain chemical reactions resulting perhaps in the formation of small quantities of 'oxyhydrate' which is described by Emley as 'a hard, gritty, yellowish material which shows a tendency to crystallize.' . . . . . .

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32 - Holmes, M. E., and Fink, G.J., Fundamental Properties of Commercial Limes; II - The Settling of Milk of Lime Suspensions: Chem. and Met. Eng., vol. 27, Dec. 20, 1922, pp. 1212-1216.

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It will also be noted that the differences between the settling rates of hydrates are much less than the differences between the rates of settling of the freshly slaked material. Slaking with excess of water brings out the individual characteristics of the limes in this respect, while mechanical hydration tends to smooth out or reduce these differences. Extreme conditions in the rate of settling are therefore best obtainable with quicklime. On the other hand, the use of hydrated limes will result in greater uniformity. . . . . .

The differences between the slaked magnesium limes and corresponding hydrates are much less than in the case of the calcium limes. The conditions obtaining in the mechanical hydration and storage, as compared with the slaking process, are probably more favorable for hydration of the magnesia, thereby minimizing the difference in the degree of dispersion and settling rate of the magnesium limes.

Knibbs[33] discusses the general influence of chemical composition. He shows that when more neutralization only is desired, magnesia is more effective than lime:

The impurities commonly present in ordinary lime are silica, alumina, iron oxide, sulphate and magnesia. In many reactions magnesia is as effective as calcium oxide, and therefore it does not come under quite the same catagory as the other impurities . . . . . .

All the above-mentioned impurities except magnesia combine with calcium oxide, and silica and alumina which may not be combined with limestone generally combine completely with the lime during calcination. The composition of the compounds formed are not easy to determine, but they are generally assumed to be 3 $CaO \cdot SiO_2$, 2 $CaO \cdot Al_2O_3$, and 2 $CaO \cdot Fe_2O_3$. It is probable, however, that even more basic compounds than these are actually present in the lime, and this supposition receives support from the fact that the 'available lime' estimated in the usual manner . . . . . , is not a measure of the value of a lime in all reactions, but in reactions such as those of water softening, sugar refining, causticizing, carbon dioxide absorption, and in general where there is no strong acid-radical involved it fairly correctly reveals its true value. When a strong acid radical is present the compound of calcium oxide with silica, alumina, or iron oxide is generally attacked to some extent, and the percentage of lime actually reacting is greater than the 'available lime' obtained by analysis.

In many reactions magnesia is as effective as lime, and, in fact, weight for weight, it is more effective because of its lower equivalent weight. For example, where the lime is used merely to neutralize acid or where it is employed as a carrier, as in the sulphite liquor used in paper manufacture, the presence of magnesia is not detrimental. In the majority of its chemical uses, however, magnesia is either much less effective than lime (e. g. in causticizing soda) or is undesirable in the product made (e. g. in bleaching powder) or both.

33 - Knibbs, N. V. S., Page 219 of work cited.

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The effect of incomplete calcination varies with different limes. A core or yolk of unburnt stone may remain intact after slaking, or it may break up partially or completely and contaminate the hydrate. It is important to use a lime in which the unburnt core, if there is any, remains intact for manufacturing of bleaching powder and other purposes in which low carbon dioxide content of the hydrate is desired.

Going further with the chemical properties of magnesium oxide, Knibbs[34] states:

> The properties of the hydroxide have not been much studied. In general it behaves like calcium hydroxide but it is a weaker base and is much less soluble. It combines with carbon dioxide and acids in the same way as calcium hydroxide but with less avidity. A suspension of magnesia in water (milk of magnesia) absorbs sulphur dioxide and hydrogen sulphide . . . .

Although there seems to be some disagreement among authorities as to the proper method of hydration, they agree that the product is influenced by the method of adding water; and in general, they favor hydration with an excess of water over that required by theory. The advantages and disadvantages of magnesium in hydrated lime will receive further consideration.

LIME IN WATER TREATMENT

The purification of water by lime affords a study of chemical reactions that the ore-dressing engineer has to take into consideration when he uses lime in flotation. Lime will relieve temporary hardness by breaking up the bicarbonates, and soda ash will precipitate the ions of calcium and magnesium that remain as sulphates. This does not entirely purify the water because sodium sulphate is left in solution. The following excerpt from the National Lime Association bulletin[35] gives a more complete presentation of the chemistry and practice:

> The elements of calcium and magnesium, in combination mainly as carbonates and sulphates, with small amounts of chlorides and nitrates, are responsible for the hardness of water. This hardness becomes objectionable when the salts are present in amounts sufficient to form a curd with soap, and a scale when the water is heated or evaporated.
>
> Calcium carbonate and magnesium carbonate are practically insoluble in water, but since all neutral waters carry the gas-carbon dioxide, the weak carbonic acid which forms when CO_2 comes into contact with water, is capable of dissolving and holding in solution these carbonates of calcium and magnesium to produce the bicarbonates, or what is known as the 'temporary hardness' of water.
>
> The water is softened by the removal of the carbonic acid either by heating, which is not a practical method, or by the addition of lime. When lime is added to waters containing dissolved limestone,

34 - Knibbs, N. V. S., Page 74 of work cited.
35 - See footnote 5.

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it will absorb the carbon dioxide which holds it in solution, the lime itself being changed back to calcium carbonate, or limestone. The limestone so formed, as well as that originally found in the water, being deprived of their solvent, carbon dioxide, both become insoluble, settle out of the water and are removed as sludge.

Magnesium carbonate is slightly soluble in water and must therefore be converted to the more insoluble magnesium hydroxide before it can be properly precipitated. This reaction is brought about by adding additional lime, which produces magnesium hydroxide and calcium carbonate, both of which are insoluble and easily removed.

The sulphates of calcium and magnesium, known respectively as gypsum and Epsom salts, are both soluble in water and require the addition of soda ash, or sodium carbonate, for their removal. They produce what is called 'permanent hardness.' The soda ash, by effecting a double decomposition of the soluble sulphates, removes the calcium and magnesium by precipitation as carbonates, leaving the soluble sodium sulphate, which does not cause hardness, in the water. The small amounts of chlorides and nitrates which may be present are removed along with the sulphates.

It may be added that lime neutralizes acid, precipitates ferric sulphate, hastens the oxidation of ferrous sulphate, which in turn is precipitated. Organic matter inherent in the water is likely to be carried down by the precipitates.

Of interest to those who are confronted with the problem of liming mine waters containing iron salts is the observation that ferrous sulphate accelerates the purifying effect of lime. The main purpose of the booklet by the American Steel and Wire Co.,[36] already mentioned, is to promote ferrous sulphate as a purifier. It deals with water purification in a broad and thorough manner. The reading of the following excerpt from the section on "Alkalinities" may well be followed by a thorough study of the booklet:

. . . . . It will be seen that alkalinity may be of three kinds, either caustic, monocarbonate or bicarbonate; that a caustic alkalinity will give a pink color to a phenolphthaleine test solution, and that the same color will be developed by a monocarbonate alkalinity, and that therefore the fact that a water turns pink when phenolphthaleine is added does not necessarily mean that caustics are present. Thus a water may have only a caustic alkalinity or the alkalinity may be wholly monocarbonate in type or it may be a mixture of the two. Or it may be wholly of a bicarbonate type or a mixture of bicarbonate and monocarbonate alkalinity. A caustic alkalinity and a bicarbonate alkalinity cannot, however, exist in the same water, and where free carbon dioxide is found neither caustic nor monocarbonate alkalinity will be present.

From the preceding it follows that six possible conditions of alkalinity might arise. The operator must be able to determine which one of these actually exists in any given water. He must also be able to

36 - See footnote 15, page 92 of work cited.

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tell just how much of any type of alkalinity is present in any water as well as the total combined alkalinity of all types present.

These six possible conditions are as follows:

I. When caustic alkalinity only is present.

II. When monocarbonate alkalinity only is present.

III. When bicarbonate alkalinity only is present.

IV. When a mixture of caustic and monocarbonate alkalinity exists.

V. When a mixture of monocarbonate and bicarbonate alkalinity exists.

VI. When a mixture of bicarbonate alkalinity and free carbonic acid exists.

Some flotation reagents will permit the use of a variety of waters, for example, some alkaline reagents are known to work almost as well in acid as in alkaline water, but generally the chemical condition of the water has to be controlled between narrow limits. An example of the necessity of precise water treatment is the conditioning of water for soap as a flotation reagent. Oleic acid and the oleates are the most common reagents for the nonsulphides, and it is well known that they are made inert by hard water. The frequent references in the flotation literature to the degree of alkalinity indicate that a thorough knowledge of water treatment is required; lime is the outstanding reagent for this purpose.

LIME IN CYANIDING

Lime from Limestone

One of the principal determinants of the use of lime in ore dressing has been its abundance and cheapness. In some cases its purpose could be accomplished somewhat more efficiently by the use of a more expensive alkali, but the additional cost is not merited. In other cases the chemical properties of lime are more desirable than those of other alkalies.

It is not unlikely that the first extensive use of lime in ore dressing was in the cyanidation process, or in connection with it. At least we know that it was used extensively for two purposes, namely, neutralizing acid and settling slime. Its function in cyanidation is summarized by Clennell.[37]

> Lime is universally used as a neutralizing agent, and is frequently added in the battery to counteract the effect of soluble acid salts in the mill or mine water; it is also used as a coagulating agent in bringing about the settlement of slimes. It is added to the cyanide solution as a protection against the soluble and insoluble cyanicides in the material treated, and also against atmospheric carbonic acid . . . . . .

37 - Clennell, J. E., The Cyanide Handbook; New York, 1915, p. 537.

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Since slime treatment is conducted at a higher pulp density than is often obtained from the milling operations, there must be a dewatering of the pulp between the mill proper and the cyanide plant. Such dewatering is accomplished by settling and decantation, but owing to the presence of amorphous clayey matter, it is often impossible to settle the pulp and obtain a clear overflow without adding some substance which will cause coagulation or flocculation of the clayey material. Hamilton[38] says about coagulation:

> . . . . . The substance most commonly used for this purpose is lime both on account of its cheapness and also because of its usefulness as an alkaline protector for the cyanide. Many other substances have a similar effect though varying in degree, such as alum, calcium carbonate, sulphuric acid, ferrous and ferric sulphate, and calcium sulphate. Lime usually forms a coarser grained and more flocculent curd with a more brilliantly clear supernatant liquor than any other electrolyte, but the precipitated mass does not settle as densely as that produced by some of the others . . . . . .

Hofman[39] explains the precipitating action of lime by discussing the coagulating power of electrolytes:

> . . . . . Coming to slimes proper, they may be said to consist of three classes of substances: Suspension, colloidal suspensions, and colloids (= pectoids of Cushman-Hubbard). A suspension is a finely divided substance stirred up in water, which will settle out gradually when left in repose; the addition of an electrolyte to the water has no effect upon the settling; the solid matter recovered by evaporating the water shows no change in its physical properties; the solid matter can be separated from the water by filtration. A colloid represents suspended particles which by carrying positive or negative electric charges repel one another continuously and thus counteract the clarifying force of gravity; the addition of an electrolyte neutralizing the electric charges causes the particles to coagulate, whereupon they settle out and carry down with them ordinary suspensions; the solid matter recovered by evaporation has lost its colloidal properties; the solid matter cannot be separated by filtration. A colloidal suspension represents a transition stage between the two extremes, and slimes belong to this category. As far as practical purposes are concerned, a slime may be defined as a colloidal suspension of finely crushed ore after 48 hours repose.
>
> The coagulating power of an electrolyte depends upon the valency of the kation. With the value of a univalent kation equal 1, that of a bivalent is 30 to 40, that of a trivalent 500 to 1,000. If 1 part FeO-salt settles 2,000 parts slimy water, 1 part Fe_2O_3-salt will settle 60,000 parts; 1 part CaO settles 1,500 to 1,800 parts. The figures "in the table below" give the relative weights required to produce the same coagulating effects.

38 - Hamilton, E. M., Manual of Cyanidation: New York, 1920, p. 76.
39 - Hofman, H. O., General Metallurgy: New York, 1913, pp. 506-507.

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Table . . . Efficiencies of various coagulating substances[1]

Substance	Relative Efficiency	Substance	Relative Efficiency
Aluminum sulphate	100	Alum (pot. chrom.)	858
Alum (potash)	143	Calcium chloride	1,095
Ferric iron	223	Calcium carbonate	1,215
Alum (ammonium)	252	Calcium sulphate	2,870
Alum (am. chrom. iron)	295	Magnesium sulphate	3,460
Lime	654	Sodium chloride	45,900
Magnesia	748	Sodium sulphate	61,700

1 - Julian-Smart, pp. 212, 220.

Fortunately, sodium sulphate, which is one of the most common by-products of water treatment, stands at the end of the list, showing that its coagulating power is not great.

Richard Meade[40] discusses hydrated lime as ideal material for use in cyanidation:

> There has been introduced in the lime trade, within the past few years, dry, slaked lime under the trade name 'hydrated lime'. This is simply calcium hydrate $Ca(OH)_2$, or in the case of certain limes, a mixture of calcium hydrate and magnesium hydrate, $Ca(OH)_2$ $Mg(OH)_2$. It is lime slaked with just enough water to convert it to hydrate without having an excess of moisture. When lime is slaked in the usual manner, water is added in considerable excess. This excess remains after the lime has slaked and forms it into a paste or putty. In the manufacture of hydrated lime, however, just sufficient water is added to slake the lime, and what small excess is employed is evaporated by the heat generated by the slaking process.
>
> There are a number of points of superiority possessed by hydrated lime over quicklime which make it peculiarly adapted to the use of cyanide plants. It has splendid keeping qualities and may be kept for several months without appreciable loss of value. There is absolutely no danger of fire from it, and it may be stored in wooden bins or even paper or cloth bags without any risk. It is extremely fine; 90% of it will usually pass a 200 mesh screen . . . . . Hydrated lime is usually purer than lump lime, because in the process of manufacture impurities are screened out.
>
> On the other hand, of course, hydrated lime contains water, and hence a given amount will not contain as much calcium oxide as will the same amount of quicklime . . . . . .
>
> Generally speaking, hydrated lime is much purer than lump lime. This is particularly true of hydrates made by the air separator process.

40 - Meade, Richard K., Hydrated Lime for Cyaniding: Eng. and Min. Jour., vol. 98, July 11, 1914, pp. 52-53.

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> In hydrates made by this method, the impurities are separated from the hydrate. These impurities consist of ashes, siliceous cores, unburned limestone and a small amount of unhydrated lime, the latter usually occurring from the over-burning and semifusing of lime . . .
> . . . . . .

Meade's article shows that hydrated lime came to the cyanide industry before the year 1914 and that its properties were appreciated. Lime from dolomite will next be considered.

Lime From Dolomite

The Engineering and Mining Journal[41] gives the following discussion of various alkalies and the advantages and disadvantages of each. The discussion was prepared before lime came into use in flotation. It directs attention to magnesia and shows that an excess gives only a faint alkalinity.

> The problem of the neutralization of acid mine water has received only slight consideration, and a valuable agent, which promises to prove much more successful than lime (CaO) or carbonate of soda (Na_2CO_3), has been overlooked. This is magnesia (MgO). In using magnesite as a water purifier, the following facts may prove interesting: The combined weights of the substances (taking them all as normal) are: Sulphuric acid (H_2SO_4), 49; lime (CaO), 28; carbonate of soda (Na_2CO_3), 53, magnesia (MgO), 20. This shows that the theoretical amount of the alkalies required to neutralize 49 parts of sulphuric acid is: Lime, 28 parts; carbonate of soda, 53 parts; magnesia, 20 parts. It will be noted that in theory the magnesia is considerably more efficient, weight for weight, than either lime or soda. In practice this superiority is even more marked. Soda is superior to lime, owing to its greater solubility although theoretically lime is nearly twice as efficient as the soda.
>
> Sulphate of soda or Glauber's salt has an additional advantage over lime, owing to this solubility of its product; it does not precipitate and choke pipes, as the almost insoluble sulphate of lime (gypsum) does. The advantages of magnesia over lime are the same as those of soda, the sulphate of magnesia formed being very soluble. It has also an advantage over soda, magnesia being very insoluble in water, whereas carbonate of soda is readily soluble, thus causing loss in working. This advantage is apparent in practical working when a considerable excess of magnesia can be used to insure the complete neutralization without troubling to make careful tests of the acidity of the water, and this without any appreciable loss of magnesite. If the neutralization is carried out by causing the acid water to flow through a bed of calcined magnesite in lumps of suitable size, the work could be entrusted to an unskilled white man or even to a native, without danger of either incomplete neutralization or loss of magnesia,

41 - Engineering and Mining Journal, Neutralizing Acid Mine Waters: vol. 107, Mar. 15, 1919, p. 478. (Abstracted from So. African Min. Jour. and Eng. Rec., Dec. 14, 1918, p. 314).

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it being merely necessary to replace the magnesite as it is dissolved away. When an excess of soda is used, this excess is lost, owing to its being dissolved unchanged and carried away. In addition to this, it will be noted from the combining weights that magnesia is more than 2.5 times as effective as soda, and as in practice 75 per cent carbonate of soda is found more efficient than lime, it follows that calcined magnesite, which can be easily obtained of a purity of from 90 to 95%, is more than three times as effective as lime.

Calcined magnesite has another advantage over crude carbonate of soda, inasmuch as it can easily be obtained practically free from organic impurities, whereas crude soda contains these to a considerable extent, and it is a well-known fact that even small quantities of organic matter in cyanide solutions interfere with the precipitation of gold in the extractor boxes. Calcined magnesite readily combines with sulphuric acid, even in dilute solution. . . . . .

Thus it is seen that MgO should not be tabooed entirely in ore dressing; it is the most active neutralizer of free acid.

The effects of magnesia in lime for the cyanidation process have been studied by Leaver and associates.[42] The results of their experiments indicated the following:

(a) In regular cyanide practice where cyanide solution is to be used repeatedly for extracting fresh batches of ore, the MgO content of calcined dolomite cannot be used advantageously to neutralize acidity.

(1) Where an excess of calcined dolomite is used to prevent the building up of magnesium salts in solution, the MgO content takes no part in the reaction.

(2) If just enough calcined dolomite is used to neutralize acidity, magnesium salts will build up and eventually form a saturated solution in which the cyanide loss would be high unless an unusual amount of 'bleeder' solution is run to waste.

(b) In the cyanide treatment of certain ores calcined dolomite may be substituted for lime with profit.

(1) Calcined dolomite is as effective as lime in preventing cyanide loss.

(2) Calcined dolomite nearly parallels lime in its precipitating and settling effect and causes no difficulty in filtration of the solution, or in the precipitation of silver by zinc.

(3) Calcined dolomite equals lime in the quantity of precious metals recovered.

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42 - Leaver, E. S., Davis, C. W., and Woolf, J. A., Calcined Dolomite as a Substitute for Lime in the Recovery of Gold and Silver by the Cyanide Process: Report of Investigation 2648, Bureau of Mines, 1924, p. 7.

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(c) In treating certain ores by the cyanide process, the recovery of silver with the use of calcined dolomite as an alkaline agent is not equal to that obtained with the use of lime.

(d) The use of MgO content of calcined dolomite would therefore be confined to neutralizing acidity and aiding settlement where the ore is crushed in water for amalgamation prior to cyanide treatment and in cyanide practice where the solution could be discarded or 'bled' sufficiently to keep down excess of magnesium salts.

Calcined dolomite should not be purchased as a substitute for lime in the cyanide process without a thorough investigation as to its action on the ore to be treated and its effect on all operations connected with plant practice.

Because of the insolubility of magnesium hydrate and the solubility of magnesium sulphate the efficient use of dolomite is restricted. Except for special and well understood conditions, lime is safer.

LIME IN AMALGAMATION

Another use of lime which was developed through the cyanide process is the use of lime in amalgamation. When milling is done in cyanide solution all of the lime is usually added to the ore before it enters the grinding mill. The lime is pulverized and mixed with the ore and thus gives the protective alkalinity that is desired. Milling in pure water is seldom done except when amalgamation precedes cyanidation. Even in this case, lime is often added to the mill. When this method was adopted mill men objected on the basis that it would harden the amalgam. However, in some cases, due to the improved amalgamation of fine gold in the slime, a marked increase occurred in the amount of gold recovered on the plates.

Clennell[43] says of wet stamp mill operation, under the caption of "Application of Lime in Preparatory Treatment of Slimes:"

> In modern practice a certain amount of lime is usually added in the battery, sufficient to dissolve any grease from the crushing machinery which might fine its way onto the plates. This has the further effect of coagulating the slime and thus bringing it into more intimate contact with the amalgamated surface. Hence it has been observed that where lime is used in the battery, the extraction by amalgamation is higher, and the assay value of the slimy portion of the tailing is lower than when the same ore is crushed without the addition of lime . . . . . .

Since lubricating oil or grease is harmful in flotation as well as amalgamation, the use of lime as a "solvent" for grease, as suggested by Clennell, may be borne in mind. Although lime is not a true solvent for grease, it causes grease to form a less harmful emulsion.

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43 - Clennell, J. E., Page 189 of work cited.

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LIME IN FLOTATION

Lime Replaces Acid Circuit

Notable changes have been made in the flotation process in the past six years. The changes that have taken place are discussed by Thomas, Christmann, and Gifford:[44]

> The outstanding developments, prior to 1923, of the flotation process related particularly to improvement in the mechanics of the process. Reagents and their properties received minor attention. The circuits employed were usually of acid reaction, and flotation of the sulphides into a bulk concentrate was the object. This period of flotation may be termed the period of 'oil flotation.'
>
> The year 1923 marked the beginning of a new period in flotation, the period of 'chemical flotation.' Well characterized compounds such as copper sulphate, potassium xanthate, thiocarbanalid, and cyanide were substituted for the oil mixtures of the preceding period. A general substitution of the alkaline for the acid circuit occurred. The outstanding characteristics of these two periods in the evolution of the flotation process are:

Prior to 1923	1 9 2 3
Oil flotation	Chemical flotation
Acid circuits	Alkaline circuits
Bulk concentration	Selective concentration.

Taggart[45] has the following to say about the abandonment of the acid circuit and the adoption of the alkaline circuit:

> Until within the last few years a majority of flotation operations were performed in acid pulps. At present, however, nearly all flotation is carried on in slightly alkaline pulps, as these are best for the chemical collecting agents. The change has effected large operating economies, since acid pulps, with copper ores particularly, were destructive of all iron with which they came into contact.

During 1923 coal tars and creosotes were the heavy oils most used in the flotation of copper ores, with pine oil as the frothing agent. The general practice was to use sulphuric acid and petroleum acid sludge to form acid circuits. The practice of acid circuits was, however, on the decline. Thomas Varley[46] writes:

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44 - Thomas, George C., Christmann, L.J., and Gifford, R. S., Hydrogen Ion Concentration - Its Control in the Flotation Process: Tech. Paper 11, American Cyanamid Co., New York , Jan., 1928, p. 1.

45 - Taggart, Arthur F., Handbook of Ore Dressing: New York, 1927, p. 845.

46 - Varley, Thomas, Consumption of Reagents Used in Flotation, 1923-1924: Report of Investigation 2709, Bureau of Mines, Oct., 1925, p. 6.

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It might be said that during the latter part of the year 1924, flotation practice was undergoing a somewhat radical change, and many plants operated experimental units using alkaline circuits together with soluble frothing reagents, such as xanthates. As a result many have altered their practices materially, and at the present time great progress in metallurgical efficiency is being made.

Differential flotation practice, or the flotation of one mineral from another or others in the presence of gangue, is rapidly being perfected. This is done not alone by the use of oils and acids or alkaline reagents but by chemicals and modifying agents which are positive in their reactions on certain sulphide minerals while others are unaffected. Advantage is taken of these facts, and chemical combinations can be added which retard certain minerals very materially in their degree of floatability. It is desirable, of course, to retard undesirable minerals such as pyrite, and exclude them from lead and zinc minerals as well as from copper minerals, where the 'dropping' of pyrite can be effected without a sacrifice of a material amount of the desirable minerals.

Varley, again, for 1925[47] writes on the increased use of modifying reagents:

In order to counteract the objectionable soluble materials present either in the ore or mill water, modifying reagents are used to 'condition the pulp' and by neutralization prevent interference of such soluble materials. Reagents of this type are soda ash, sodium silicate, sodium sulphite, crude soda, lime, and acids. In this connection lime is generally regarded as a 'chemical,' on account of its action on the minerals, and its reactions with acidic solutions or soluble salts in ore.

The year 1925 saw the passing from acid to alkaline circuits. Chemical flotation agents and conditioning agents have proved far more effective when used in alkaline pulps. Lime, as compared with acid, is much cheaper, and can be handled and stored much more easily and safely than acid. Lime can be manufactured in almost any locality, and procured more readily than acid. Nearly all the big operators have their own lime plants now and several are manufacturing their own reagents.

The following table, compiled from data given in Reports of Investigations[48] of the United States Bureau of Mines shows the increased use of lime in flotation and also the general statistics of flotation operations. By comparing this table with Table 1, one can see that in 1928 flotation consumed 2.5 per cent of the total lime produced.

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47 - Varley, Thomas, Consumption of Reagents Used in Flotation, 1925; Report of Investigation 2777, Bureau of Mines, Oct., 1926, p. 2.

48 - U. S. Bureau of Mines Reports of Investigations as follows: No. 2203 for 1919; No. 2709 for 1923-24; No. 2777 for 1925; No. 2852 for 1926; No. 2931 for 1927; and No. 3004 for 1928.

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Table 4. - Consumption of reagents used in flotation for the years 1919, and 1923 to 1928, incl.

Year	Tons treated by flotation	Ratio of concentrates	Pounds of lime	Pounds of reagents	Pounds of reagents per ton of feed
1919	26,545,564	8.55	1/1,570,200	113,510,234	4.2384
1923	37,811,044	13.04	2/2,422,491	161,377,789	4.2680
1924	45,105,101	15.28	2/2,053,600	178,699,681	3.9618
1925	45,490,331	16.301	2,166,819	81,666,967	1.7952
1926	50,889,254	15.177	162,240,359	201,711,795	3.963
1927	50,073,450	-	169,926,145	220,514,373	4.404
1928	59,064,385	-	208,249,403	264,033,473	4.470

1/ Kind not stated.
2/ For copper ores only.

An increase in the ratio of concentration followed the general adoption of the alkaline circuit. In 1919 the average ratio of concentration with the acid circuits was 8.55; for the following years the ratio of concentration in alkaline circuits was practically doubled. A slight decrease in later years, from 15.28 (on copper ores largely) may be due to the treatment of an increased tonnage in lead-zinc-iron ores.

With the almost universal adoption of the alkaline flotation circuits and in view of the abundance and geographic distribution of limestone from which lime is obtained, it is not to be wondered at that lime finds such extensive usage.

Weinig and Palmer[49] add the following on this subject:

> Lime is the most used alkaline reagent, because of its cheapness and availability. Caustic soda and caustic potash could be used to replace lime in many cases, but they are much more expensive . . . .

Concerning the wide usage of lime in flotation, Thomas[50] and his associates write:

> Since the abandonment of the strongly acid solutions in the flotation of copper, the lime circuit has been adopted almost universally . . . . . .

The full significance of the statement is realized when it is remembered that of the 50,073,450 tons of ore treated by flotation in 1927, 40,881,768 tons of copper ores, making only one concentrate, were treated. In 1928 more than 99 per cent of the copper ore milled was treated in alkaline circuits using lime.[51]

49 - Weinig, Arthur J., and Palmer, Irving A., The Trend of Flotation: Quar. Colorado Sch. of Mines, vol. 24, No. 4, Golden, Colorado, Oct., 1929, p.22.
50 - Thomas, G. C., Christmann, L. J., and Gifford, R. S., page 4 of work cited.
51 - Miller, T. H., and Kidd, R. L., Flotation Reagents, 1928: Report of Investigations 3004, Bureau of Mines, June, 1930, p. 6.

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Choice and Preparation of Lime for the Circuit

Since lime (CaO) plays its role in flotation in the pulp and hence in solution as $Ca(OH)_2$, it may be added to the circuit in three forms. S. E. Stein says:[52]

> Lime functions in the flotation process as calcium hydroxide, after being dissolved in the mill circuit water. It is added as (a) burnt lime--calcium oxide with other substances residual after burning of limestone, or (b) hydrated lime--dried calcium hydrate with other substances residual after the slaking of burnt lime, or (c) milk of lime--a suspension in water of particles of hydrated, or freshly slaked lime, making a mixture containing 25 per cent solids or less, depending on requirements. The water is of course saturated with respect to calcium hydroxide. Solubility of calcium oxide in distilled water, at 15° C., is 0.120 per 100.
>
> The effective portion of the added lime is that which goes into solution in the mill circuit water to react as calcium hydroxide, and its magnitude will therefore be governed primarily by the quality of the original limestone and the efficiency of the burning. Lime should, of course, be purchased on the basis of the available calcium oxide of standard analysis, as this figure has a reasonably dependable relative value; but it is worth noting that the figure thus given will usually be higher than realized in practice on account of the fact that solvent solutions in a mill circuit are not as good as those used by the chemist in his methods for this analysis.
>
> The choice between burnt lime, hydrated lime, and milk of lime will be governed by local factors. The problem to solve is that of getting the required quantity of calcium hydroxide into mill circuit solution in the cheapest way consistent with accurate control of the feed. Feeding of burnt lime or hydrated lime requires a greater refinement of mechanical control than that ordinarily used for feeding ores, if the proper flotation control is to be attained. A storage bin or hopper delivering onto a feeder of the conveyor belt type, the speed of which is controlled by a rachet mechanism, variable cone pulley, or variable speed motor has been used successfully where the feed from bin to belt could be maintained with respect to range of sizes. Milk of lime offers a surer feed control, and for that reason has been adopted at plants where the highest order of metallurgical results are demanded. For feeding milk of lime a storage tank equipped with means for maintaining the calcium hydrate particles in suspension is required, as well as variable-control fluid feeder.
>
> The adverse factor in burnt lime is the fire hazard wherever water shipment or long time storage is required, or air slaking in the latter case . . . . . In most cases the payment of higher

52 - Stein, S. E., Lime in Flotation: Eng. and Min. Jour., vol. 125, Mar. 24, 1928, p. 487.

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prices for hydrated lime will be found unwarranted, as a fairly good grade of burnt lime is usually available at the same source, from which a unit quantity of calcium hydroxide can be furnished to the mill circuit more cheaply than can be so furnished by the hydrated lime.

Robie[53] writes of one company's method of handling lime:

Lime now being used extensively in the mill (about seven tons a day), apparatus for its local manufacture was installed some years ago. A kiln was constructed out of the old steel stack at the Shannon smelter, in Clifton. A good grade of limestone is available near by, and the entire operation of quarrying the stone and making the lime costs only about $6 per ton. About a quarter of a ton of fuel is required per ton of product. This contains about 90 per cent of total calcium oxide, and about 85 per cent of available. The burnt lime is crushed to 3/4-inch, stored in a steel bin which is drawn as required, and ground in the first Marathon mill that was ever made, secured from the old plant of the Detroit Copper Mining Company in the vicinity. Balls have been substituted for the rods originally used in this mill. The grinding is carried out in a closed milk-of-lime-circuit, the requisite supply for the concentrator being drawn off from the tank containing the circulating solution and introduced into the pulp at the following points: The primary screen undersize, the grinding mill feed, and in the concentrate and tailing launder. Arrangements were being made at the time of my visit to treat fresh water with lime directly as it comes from the kiln, eliminating the storage of unslaked lime.

Porter[54] gives the advantages of the use of hydrated lime as follows:

The chief advantages to the consumer of hydrated lime are as follows: It can be handled more easily on account of its being in powder form; it will keep better than the lump lime for the reasons just noted; it does not require slaking, but must merely be soaked in water to prepare it for use. This saves time and labor and eliminates any danger of loss of lime due to unskilled slaking. Any unburned lime or overburned lime which has passed the sorter will not hydrate and can be screened out of the finished product. Hence hydrated lime should contain less refuse than the lump lime. On the other hand, hydrated lime contains 15 to 25 per cent of water, on which the consumer may pay freight.

Henderson[55] condemns dolomite and gives the following discussion on the use of lime to alkalize mill circuits:

. . . . . The question often arises as to whether calcined dolomite may not be substituted for strictly calcium lime for flotation purposes: There is but one answer, and that is the negative.

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53 - Robie, E. H., The Morenci Concentrator of the Phelps Dodge Corporation: Eng. and Min. Jour., vol. 126, Aug. 25, 1928, p. 293.
54 - Porter, J. M., Page 13 of work cited.
55 - Henderson, Clark T., The Proper Use of Lime to Alkalize Mill Circuits: Eng. and Min. Jour., vol. 120, Dec. 26, 1925, p. 1016.

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The reason for this is that the lime, to be effective, must go into solution in the pulp, and magnesium hydroxide is scarcely soluble in water, so that if dolomitic lime is used, only the calcium hydroxide contained is useful for flotation purposes and much larger quantities must be employed.

Though lime is one of the commonest chemicals and seemingly one of the simplest, it has peculiar characteristics worthy of serious consideration in using it in flotation. As already stated, the calcium hydroxide must go into solution to be effective. A part of the lime which goes into solution is consumed in neutralizing the temporary hardness of the water used in making the pulp; more of the lime is consumed in neutralizing such acidity as there may be in the ore, and the balance creates the necessary alkaline condition in the circuit.

It is common practice in some plants to feed lime into the flotation circuit as dry quicklime, or calcium oxide. If fed thus, the conditions under which the quicklime will slake are quite uncertain, and the conditions under which the lime is slaked have a distinct bearing on its effectiveness in the flotation circuit. Other plants use hydrated lime, which is quicklime slaked with the theoretical amount of water required for hydration. This hydrated lime is either fed dry into the flotation circuit or is mixed with water to form milk of lime, which is then fed into the circuit. Still other plants make a practice of slaking quicklime with uncertain quantities of water, when making up a milk of lime of uniform strength for feeding into the flotation circuit.

A comprehensive series of experiments that were conducted in our company's laboratory gave the following results:

Where a certain amount of quicklime was slaked with the theoretical amount of water required for hydration; this hydrated lime then diluted with additional water to a standard volume; and this standard volume of milk of lime placed in a graduated cylinder, thoroughly agitated, and allowed to settle, the time required for the undissolved material to settle to 50 per cent of the total volume of the original milk of lime was 10 minutes. A corresponding sample of quicklime was next taken and slaked with 10 times the theoretical amount of water required for hydration. This was then diluted to standard volume, placed in a graduated cylinder, thoroughly agitated, and allowed to settle. The time required for the solids to settle to 50 per cent of the original volume was in this case 440 minutes.

It was obvious from the foregoing and other experiments that lime slaked with not less than 10 times the theoretical amount of water is much slower settling and consequently much easier to hold in suspension in the feed tanks, and has less tendency to settle out in the flotation circuit, than milk of lime made of hydrated lime, or quicklime slaked with small quantities of water.

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Having thus proved that an excess of water gives a milk of lime having a lower settling rate, experiments were next undertaken to determine the relative chemical activity of these two types of milk of lime. Each sample of milk of lime was thoroughly mixed with the theoretical quantity of sodium carbonate that would react therewith to form calcium carbonate and sodium hydroxide. The relative time required for causticizing was taken as an index of the relative chemical activity of the two types of milk of lime. The milk of lime which settled in 10 minutes was found to require 330 minutes to effect complete causticizing of soda ash mixed therewith, whereas the milk of lime requiring 440 minutes to settle was found to react completely with soda ash in 5 minutes.

The foregoing experiments seem to prove beyond question that the proper type of milk of lime to use in flotation work is one made by slaking high calcium quicklime with not less than 10 times the theoretical amount of water required for hydration, because a milk of lime so made is not only slow settling but much more active in a chemical sense. The same conclusions would seem to apply to the use of lime to secure protective alkalinity in cyanidation.

Here, as in the section on "Hydration," the use of an excess of water in the preparation of the hydrate is recommended; and the evidence indicates that the hydrate made in this manner is much more finely divided. It is not, however, always practical for the operator to slake his own lime, in which case a good grade of hydrate may be used very effectively.

Place of Adding Lime

Lime may be added to a mill circuit in any of a number of places, or even in several places in the same circuit. Ralston and Yundt[56] point out the necessity of adding lime to the pulp far ahead of the flotation machines:

> . . . . . It is probable that in the cases noted where lime improves flotation it functions in precipitating other less desirable soluble impurities, such as iron sulphates. At the Miami mill it was found that when lime was added to the pulp before entering the ball mills an increased recovery was obtained, whereas the addition of lime at the head of the flotation cells resulted disastrously. Supposedly the lime had to be allowed time enough to react with all the soluble or semi-soluble impurities in the pulp before going to the flotation machine, so that there would be no raw caustic lime to cause trouble.

Robie[57] states that at Morenci ground milk of lime is added to the primary screen undersize, the grinding mill feed, in the concentrates and tailings launder, and to the fresh water as it comes from the mine.

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56 - Ralston, O. C., and Yundt, L. D., Chemicals Used in Flotation; Min. Sci. Press, vol. 115, Oct. 13, 1917, p. 547.

57 - Robie, E. H., Page 293 of work cited.

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Tye[58] reports adding milk of lime and a small stream of tailings to the mill water supply, so that the impurities are precipitated as gelatinous salts which are buried by the slime and sand of the tailings. To overcome the effect of soluble salts in the ore and obtain the desired alkalinity for flotation, more lime is added at the rod mill.

MacDonald[59] cites an instance where "dry lime is fed mechanically onto the ore conveyors . . . to the primary mills."

McDermid[60] in a recent article discusses the new practice at the Miami Copper concentrator where they

> . . . . . emulsify the lime first and then pump it to the mill pond, where the insoluble material would have a chance to settle out.

Regarding the removal of the precipitated impurities, he writes:

> . . . . . After some experimenting a dragline scraper was built which successfully removes the sludge from the bottom of the pond.

Commenting on the practice in the Tri-State District, Anderson writes:

> In the Tri-State District lime (hydrated) is added for its beneficial effect on flotation results at anyone of a number of places in the mill. Often it is added to the ball mill feed, sometimes to the waters going to the Dorr thickener, sometimes to the pulp passing to the head flotation circuit; occasionally it is added to the settling pond or to the mill pump, well, or lake. The general practice seems to be to add it at some place in the mill where it will have time to act and exert its effect before the pulp reaches the flotation machines. Several methods of adding lime are in use; adding by hand is practiced often, and adding by means of several homemade devices is quite prevalent. Most of these feeders are some form of hopper-like boxes in the bottom of which is a worm screw or some simple agitating device for causing the lime to flow. Recently one mill installed a continuous belt feeder which has proved very satisfactory. Very often lime is not required continuously, hence it is added one week and not the next. Lime is added usually as the hydrate.

Lime is not used much in the lead belt of southeast Missouri. If thickening capacity is limited, a little lime is used to aid settling, but caution is required lest the lime retard the flotation of lead. In the differential lead-zinc plants of the district, hydrated lime is used at the head of the zinc circuit to depress the iron. The price paid for hydrated lime is $9.40 per ton.

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58 - Tye, A. T., Differential Flotation of Copper at Cananea: Eng. and Min. Jour., vol. 121, Apr. 10, 1926, pp. 597-602.

59 - MacDonald, Wm. T., Selective Flotation at Nacozari: Eng. and Min. Jour., vol. 118, Sept. 20, 1924, pp. 445-454.

60 - McDermid, A. J., Liming Mill Water: Eng. and Min. Jour., vol. 130, Oct. 9, 1930, p. 341.

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Lime as a Purifier

The waters encountered in milling and flotation operations are often highly contaminated with soluble metallic salts and must receive special treatment to make them fit for flotation. An unusually complex water problem was encountered at Cananea (Mexico). The difficulties encountered and the method of overcoming them are given in the article by Tye.[61]

> Differential flotation of a copper ore containing large amounts of pyrite offers no unusual difficulties when the ore is unoxidized and when fresh water is available. At Cananea, however, several elements unit to interfere with the process, and therefore the following account will deal principally with these unusual features and give in detail the methods used in overcoming them . . . . . .
>
> The following analyses show the effect of lime on the treatment of dam water, a sample of which was made alkaline by the addition of lime, using phenophthalein as indicator:

Dam Water Analyses in Parts Per Million

	Ferrous	Ferric	CaO	So_3	Cu	Alkalinity (CaO)
Dam water	400	200	470	2,270	28	(Neutral to (phenol-
Same, treated and filtered	Tr.	Tr.	1,420	2,106	17	(phthal- (ein

> The precipitate gave the following analysis in per cent: Fe, 20; S, 5.8; Mn, 11.0; Cu, 16.5; CaO, 3.4; SiO_2, 3.2; and Al_2O_3, 3.0.
>
> One can appreciate better the real nature of this water after having seen it made alkaline with lime. At first a light yellowish flocculent precipitate develops as a small amount of lime is stirred in. Then, as the final amount of the required lime is added, the whole mass of water takes on a deep bluish-black color and the consistency of the water approaches that of thin soup. The manganese salt is the last to settle out, as a pink precipitate. Finally the floccules settle, leaving a clear liquid of the analysis shown above . . . . . .
>
> By the last of April everything was ready to try the process in the concentrator. For the first month and a half the results were quite poor, owing to the impure water. The tailing dam from which the water was drawn was filled with the impure water and the supply was augmented by the mine water, which was equally bad. The water was neutralized with lime before being used, but it still contained the precipitated iron salts, and no acceptable results could be obtained. This trouble was partly overcome by utilizing all the extra Dorr tanks, of which there were several, to settle out these precipitated salts.

61 - Tye, A. T., Work cited.

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The water for the dam was lime-treated, mixed with tailing, sent to the tanks, and the clear overflow of the latter repumped for mill water. This cut the concentrator tonnage in half, as sufficient water could not be supplied. Therefore, means were provided to add excess lime to the tailing going to the dam to purify all the water in storage, as it was realized that in this way only could the process be applied successfully. This consumed considerable time, and it was June 16 before all the storage water was purified. Since then it has been necessary to use sufficient lime to secure the desired alkalinity for flotation and also to purify the makeup water which comes from the mines. This latter is treated before it enters the tailing pond.

In the meantime, the worst mine water was being segregated and discharged outside the drainage area. The change made in the composition of the great bulk of water in the tailing pond is shown in the following analyses:

Dam Water, Parts per Million

Date	Ferrous	Ferric	Mn	CaO	Cu	SO_3	Alkalinity	Acidity
Feb. 12, 1924	600	120	50	420	42	2,559	Nil	40
June 16, 1924	Nil	Nil	Nil	1,260	Nil	1,749	50 M.O 39 P.P.	--

. . . . . When passing the concentrator, however, milk of lime is run into the arroyo water until it shows distinct alkalinity. Crushed lime is fed into a small ball mill, and a minimum amount of water added while grinding so that considerable heat is generated in the mill, the lime does not get 'drowned,' and the majority goes into solution. This is run into the middle of the stream of water to be treated, and at the same time a small stream of tailing is also discharged with the lime, so that the gelatinous salts are precipitated and the slime and sand of the tailings bury them. At a point below where the lime is added to the arroyo water, a sample is taken every hour and titrated to be certain that sufficient lime has been added.

To overcome the effect of soluble salts in the ore (and to secure the desired alkalinity for flotation), lime is added to the rod mills, the discharge from these being tested every hour. Flotation feed is titrated for alkalinity hourly . . . . . The lime used is burned locally by the company and costs $6.50 per ton . . . . . .

Best results are with an alkalinity in the flotation feed equal to about 0.55 lb. of CaO per ton of water . . . . . .

Flotation reagents used are potassium xanthate, steam-distilled pine oil, and lime, the average pounds per ton being 0.09 xanthate,

62 - Gaudin, A. M., Control of Flotation; Eng. and Min. Jour., vol. 125, Mar. 10, 1928, p. 418.

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0.23 pine oil, and 9 to 11 lime. The lime includes that used in treating the mine water and varies considerably from month to month, depending on the purity of the water and character of the ore. In extreme cases it has averaged 12.5 lb. for a month . . . . . .

Mill waters vary widely in composition from time to time, and are one of the most pertinent factors affecting the continuity of flotation results. Concerning this subject, Gaudin[62] writes:

. . . . . Variations in mill water are due to somewhat different causes, according as the mill is using fresh water or returned-circuit water. Where fresh water is used, the change in mineral and organic content is one of the big upcetting factors--particularly true in places where climatic conditions affect the amount of water available, where periods of oxidation of the ground alternate with periods of heavy precipitation. When mine water is used, variations are also likely to occur as new sections of the mine are opened up.

If the water is returned to the mill after use--where circuit water is the dominant ingredient--the water is usually more regular in its mineral content than if fresh water only is used. On the other hand excess reagents can build up rapidly under such conditions, so that accurate control of the amount of reagent is still more essential . . . . . .

McKay[63] sums up the soluble metallic salts generally present and their removal from contaminated water in the following manner:

The most common soluble metal salts are generally the salts of the minerals, including sulphates of zinc, copper, and iron; and salts derived from the gangue, such as sulphates of calcium, aluminum, and magnesium. However, in flotation circuits, many salts often thought of as insoluble enter solution in extreme dilution. The importance of even the weakest solution of such salts will be appreciated by remembering that many of our reagents--notably the promoters--are extremely effective even when present to the thousandth of a pound per ton of ore, which is equal to one part in ten million, or 10^{-7} (at 20 per cent solids). At this dilution many of the so-called insoluble salts are in solution in sufficient concentration to influence flotation conditions, so that a list of the soluble salts and also the reagents used to combat them would appear like an abbreviated chemical dictionary. The common polar reagents for destroying the toxic constituents of the ore are lime, soda ash, and sodium sulphite, sulphide, and silicate.

The simplest case of the removal of soluble salts from solution by the use of lime is in the purification of water for industrial purposes. (See section "Lime in Water Treatment.")

63 - McKay, Nevin Hall, Soluble Salts as Flotation Reagents: Eng. and Min. Jour., vol. 128, Dec. 14, 1929, pp. 920-921.

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Knibbs[64] writes of the softening of water for domestic purposes and shows that lime precipitates organic matter:

> Water for domestic purposes may also be subjected to a softening process, but it is still more important to free it from organic matter and from harmful organisms. Precipitation of the hydroxide of iron and aluminum tends to carry down the organic matter, and lime is used in this connection to neutralize acidity and effect precipitation. Lime itself may be sufficient to precipitate the bulk of the organic matter.

Hahn[65] adds the following about ferrous, ferric, and aluminum sulphates and their bearing upon copper recoveries, and their removal:

> . . . . . The influence of the salts of iron and aluminum, and methods for eliminating these effects in the flotation of copper ore have been the subject of an investigation to be summarized here . . . . . .
>
> The following deductions are drawn from the results obtained:
>
> 1. Ferrous, ferric, and aluminum sulphates seriously affect copper recoveries, even when present in relatively small amounts.
>
> 2. Burnt lime eliminates, to a large extent, the deleterious effects of ferric and aluminum sulphates, but offsets to only a small extent the effect of ferrous sulphate.
>
> 3. By adding an oxidizing agent, such as oxygen, chlorine, or chloride of lime, to the ore pulp in the presence of burnt lime, the effect of ferrous sulphate can be almost completely eliminated.

Ralston and Yundt[66] say the following about the use of calcium sulphate or the effect of it in the flotation circuit:

> Calcium sulphate is a compound which has been added to ores containing colloidal gangue, although its success has been somewhat erratic. It was once used in one of the Broken Hill mills and its effect was that of an electrolyte. It is sparingly soluble, so that there can never be a high concentration of its ions in solution and it is hence more or less equivalent to the tartrates in providing ions rather slowly, so that, supposedly, the flocculation of gangue-slime will not entrain particles of the desired mineral.

Instead of emphasizing the use of lime, McKay[67] calls attention to ferrous sulphate as a flotation reagent:

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64 - Knibbs, N. V. S., Page 272 of work cited.
65 - Hahn, A. W., Obviating the Harmful Effects of Soluble Salts in Flotation: Eng. and Min. Jour., vol. 123, Mar. 12, 1927, p. 449.
66 - Ralston, O. C., and Yundt, L. D., Page 549 of work cited.
67 - McKay, N. H., Page 921 of work cited.

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> Again, without intending to be bound by any one theory, I believe that in copper-iron separation, ferrous sulphate, generally native in the ore, plays a part analogous or parallel to the action of zinc sulphate in lead-zinc flotation. As to the end reaction of excess ferrous sulphate with xanthate, mill experiment has not yet given data to show whether iron xanthate could be used in copper-iron flotation as zinc xanthate has been used in lead-zinc separations. Apparently sulphated pyrite, which occurs in nearly all copper-iron or lead-zinc-iron flotation, does play a part in the formation of ferrous or ferric sulphates, or cyanides of ferrous or ferric iron, which act in iron depression. The practice here, therefore, has naturally developed of using commercial copperas or iron sulphate with the sodium sulphite or cyanide as a pyrite depressant, with results that have been highly gratifying, yielding again a higher-grade concentrate, higher recovery, and smoother metallurgical performance.

Another use of lime in flotation which is closely related to precipitating soluble salts is its use in producing coagulation and settling of colloidal particles of slime and the "sweeping down" of suspensions of organic colloids. This action is a physico-chemical one. Rickard and Ralston[68] discuss the subject as follows:

> A word must be devoted to the use of lime as a flocculating agent . . . . . At first sight it would appear improbable that lime could have a purely physical flocculating action, lime being an alkali and the characteristic effect of small concentrations of alkali appearing to be a deflocculation rather than the reverse. There is, nevertheless, a certain flocculating action exhibited by lime, even under laboratory conditions, and it appears that the hydroxides of calcium, and probably magnesium do not behave exactly like potassium and sodium hydroxides. It appears probable, also, that certain purely chemical factors enter as well and that the efficacy of lime as a clarifier is due in part to chemical reactions of the same sort as those that control, for instance, the action of aluminum salts in clarifying water. These clarifying actions apparently depend upon the formation by chemical reaction of some flocculent precipitate that entangles and sweeps down suspended particles. Probably the occasional cases of clarification by organic colloids belong to the same class.

Ralston and Yundt[69] add:

> Lime is not such a desirable addition-agent as the alkaline sodium compounds; and while it may cause desirable effects when added in small amounts, an excess is often harmful. Lime and most other calcium compounds are usually flocculators of gangue-slime, rather than deflocculators as the alkaline sodium compounds are. This may explain the difference between the two, although it has

68 - Rickard, T. A., and Ralston, O. C., Flotation: San Francisco, 1911, p. 320.
69 - Ralston, O. C., and Yundt, L. D., Page 547 of work cited.

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been hinted often that we know too little about the degree of flocculation of the ore-pulp during flotation . . .

The settling effect of lime is mentioned by Weinig and Palmer:[70]

> There are many factors that influence the settling rates of finely ground ores. For instance, an ore that has been air dried settles more rapidly than one coming directly from the mine. Argillaceous ores have poor settling properties. Lime and xanthate promote settling, while soda ash and sodium sulphite retard it.

Thus lime plays a multiple role as a purifier. It may be used to remove most of the impurities in water. Through chemical action it brings about the precipitation of the salts that cause temporary hardness and also precipitates many of the metallic compounds. Through physical action it facilitates the settling of suspensions and aids in the removal of organic matter.

LIME FOR ALKALINITY

The advantages of alkaline flotation circuits allow the use of an excess of lime in the purification of mill water. That which remains is active in producing alkalinity and becomes an important flotation reagent. Henderson[71] mentions the use of excess lime in solution as follows:

> . . . . . A part of the lime which goes into solution is consumed in neutralizing the temporary hardness of the water used in making the pulp; more of the lime is consumed in neutralizing such acidity as there may be in the ore, and the balance creates the necessary alkaline condition in the circuit.

Earlier in the same article Henderson says:

> Xanthate will give good results in acid circuit, but it seems more satisfactory in alkaline circuit, and the advantages of flotation in alkaline rather than acid circuit are usually such as to make the alkaline circuit preferable, even though the metallurgical results in both are the same.
>
> Alkalinity can be best secured with the aid of lime, as is done in cyaniding, the quantity required varying in practically every instance . . . . . .

The fact that the quantity required varies, makes alkalinity control important.

It is quite evident that the calcium ion and the hydroxyl ion both play a part in flotation, though the action of both is subject to uncertainty. Stein says:[72]

70 - Weinig, A. J., and Palmer, I. A., Page 43 of work cited.
71 - Henderson, C. T., Page 1016 of work cited.
72 - Stein, S. E., Page 489 of work cited.

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. . . . . It is necessary to know a great deal more about the action and effects of the calcium ion; and this may prove a difficult problem. With respect to the hydroxyl ion it is probable that experimentation with various reagents used in flotation under careful pH control will result ultimately in important advances in our knowledge.

Stein, earlier in the same article, cites two instances of the control of alkalinity.

One plant treating a fairly clean sulphide ore, as indicated by its low burnt-lime consumption of 1.5 lb. per ton of ore, used a standard of alkalinity for the flotation heading water equivalent to 0.20 lb. calcium oxide per ton ore (at 20 per cent solids). Markedly bad effects were noted when this quantity fell below 0.10 lb. CaO, but the facts are uncertain as to the intermediate range. Samples were taken at half-hour intervals.

Another plant, having a lime consumption of approximately 5 lb. per ton of ore, used a standard equivalent to 0.10 lb. CaO per ton of ore, at 20 per cent solids. Titrations were made at 15-min. intervals. The bad effects were visible to the operator when the alkalinity declined to 0.07 lb. CaO, and the appearance of a couple of '0.05's', and say, one '0.00' on the titration record sheet was an infallible sign that the corresponding assay sheet would indicate inferior metallurgical results. The effects of 'overliming' certainly were not visible to the operator until an alkalinity of 0.15 to 0.17 lb. CaO was reached, and inferior metallurgy resulted with certainty only when a considerably higher figure was reached . . . . .

Among the various ores treated at one company's plant there would occasionally be received one which laboratory tests indicated was amenable to flotation treatment, with approximately equal results, by the use of either lime, or sulphuric acid, or in a 'neutral' circuit. But the rule was that either alkaline or acid circuit, each with its special accompanying reagents, was required to produce the best obtainable metallurgy. The 'neutral' circuit would show material losses in the tailing. There is, of course, the possibility of existence of a suitable reagent for the 'neutral' circuit, but this was not discovered.

The control of alkalinity presupposes an accurate method of quantitative determination. Phenolphthalein, the indicator frequently used in cyanidation and flotation, is not sensitive toward low alkalinities. Its change in color occurs only when the solution is well on the alkaline side (pH 8.5), and the fact that it is colorless in pulps more acid makes it useless near the neutral point. It is interesting at this point to give the discussion of Thomas, Christmann, and Gifford[73] on the difference between hydrogen ion concentration and acidity as expressed in normality:

73 - Thomas, Christmann, and Gifford, Pages 2 and 3 of work cited.

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It is necessary to distinguish between the hydrogen ion concentration of a solution and its acidity as expressed in normality. A liter of normal acetic acid will, of course, neutralize the same amount of alkali as a liter of normal hydrochloric acid, but the hydrogen ion concentration in the latter solution is much greater than in the former. This is the reason for many of the differences in the properties of acetic and hydrochloric acids and is what is usually meant by the statement that hydrochloric acid is 'stronger' than acetic acid. The hydrogen ion concentration is, therefore, a measure of what might be termed the 'active acidity' of a solution rather than of the total acid concentration.

. . . It is obvious that the pH of a solution cannot be determined by titration, for this would show the total acid or alkali available for neutralization, which, as we have seen, is not a measure of the hydrogen ion concentration. Furthermore, the introduction of acid or alkali into a solution would immediately change the pH value and thereby destroy the thing to be determined.

Regarding the function of lime alkalinity, MacDonald[74] says the following:

. . . . . Lime assumes the important function of protecting xanthate by impeding its precipitation by soluble iron, though happily permitting the corresponding reaction with soluble copper. Sodium sulphide, or even an excess of sodium xanthate itself, might well serve some functions of lime, except as the wastage of these more expensive reagents by soluble iron might be intolerable. The discriminating precipitation of the latter is desirable. In a lime circuit, the relatively low solubility of calcium xanthate may be a disadvantage.

Thomas and his associates[75] add the following remarks concerning the use of aerofloat in a pulp containing high lime alkalinity:

. . . . . When used in solutions of high lime alkalinity, Aerofloat has occasionally given erratic results and this fact has led us to investigate the effect of alkalinity upon flotation, with particular reference to flotation in solutions whose reactions are very near the neutral point. . . . . .

Stein[76] adds:

. . . . . One large company that found it profitable to adopt pH control as a guide to flotation operations discovered that the correct value when using one reagent was not the best value when using another. Thus when it discontinued the use of the lime-xanthate circuit in which the correct pH value was approximately 10, it was found that the lime-aerofloat circuit, subsequently introduced, operated to best advantage when the pH was 8.3.

74 - MacDonald, Wm. T., Selective Flotation: Eng. and Min. Jour., vol. 126, Oct. 27, 1928, p. 681.
75 - Thomas, Christmann, and Gifford, Page 1 of work cited.
76 - Stein, S. E., Page 489 of work cited.

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Thomas and his co-authors[77] think that lime is not needed when cyanide is used as a depressant:

> It may be mentioned in passing that the depressor effect of cyanide is almost always brought out to the best advantage by working in solutions much on the acid side of phenolphthalein. The use of an alkali to 'protect' the cyanide, following the precedent of ordinary cyanidation, is not only unnecessary but is actually detrimental to the effect of cyanide as an iron inhibitor.

Stein[78] writes of the effect of over and underliming:

> With regard to the comparative deleterious effects of 'underliming' and 'overliming', a more thorough investigation as well as the collection of available data from diverse sources is needed. For what it may be worth, I am herewith setting forth my present impression on this subject. It is probable that the theoretically best degree of alkalinity varies for each mine, and consequently also varies with ores originating at different points in the same mine. The necessity of constant experiment is indicated.
>
> In starting operation with lime it would be wise to set the standard point of alkalinity sufficiently far in advance of neutrality--consistent with the avoidance of excessive overliming--to reduce the recurrence of complete loss of alkalinity to a minimum. 'Underliming', especially when it results in complete loss of alkalinity, is markedly harmful to metallurgical results. The froth livens up, becoming decreasingly selective in appearance as the alkalinity diminishes. If the condition is not remedied by speedy lime additions, the froth will 'run away' in spite of attempts at correction by reducing the quantity of the frothing agent. This naturally affects both the concentrate and the tailing.
>
> 'Overliming' has the reverse tendency unless carried excessively far, when a condition in outward appearance something similar to 'underliming' will take place. The first 'overliming' slows the froth down slightly, and thus has a tendency to clean up the concentrate with slight loss in the tailing. This moderate 'overliming', however, is not usually harmful, as it is easily corrected. The corresponding degree of 'underliming' usually would show a definite loss in tailing for the shift. However, at one plant which treats a variable ore, I have noted on three separate occasions the loss of a considerable quantity of the standard alkalinity, without a manifestation of the bad 'underliming' effects as described.

Thomas, Christmann, and Gifford[79] write of the amount of lime generally used and the effects:

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77 - Thomas, Christmann, and Gifford, Page 6 of work cited.
78 - Stein, S. E., Page 488 of work cired.
79 - Thomas, Christmann, and Gifford, Page 4 of work cited.

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. . . . . The amount of lime employed is generally in excess of that required to neutralize the true acidity of the ore and the resulting circuit is usually strongly alkaline toward phenolphthalein. These high alkalinities require the use of large amounts of lime, so that the cost of lime is frequently larger than that of the other reagents combined. As a reason for these high lime additions, the depressant action of lime upon flotation of pyrite is frequently cited. While it is undeniable that lime does inhibit the flotation of pyrite, the depressant action is not specific to pyrite and the advantage gained in this direction may easily be lost in others. Thus high lime alkalinity has been found detrimental to the flotation of chalcocite; it has also been found to cause irregularities in the behavior of the flotation reagents, notably of frothers.

The neutralizing and depressing effect which lime exhibits is probably the chief reason for its use as a flotation reagent.

LIME AS A DEPRESSOR

(A). Comments on Depression

There are two theories to account for the depressing action of lime: (1) The slime theory, and (2) the theory involving preferential deposition of a compound formed by the added agent and some constituent of the ore pulp other than the mineral upon which the salt is deposited (calcium carbonate theory of Gates and Jacobsen).[80]

The effect of lime in the slime theory is discussed by Taggart, Taylor, and Ince.[81]

The presence of certain soluble inorganic compounds causes amazing differences in the behavior of the gangue slimes. Thus lime in the proportion of 500 mg. per l. (equivalent to about 4.0 lbs. per ton of ore in the usual pulp) substantially prevents deposition of Anaconda slime on galena . . . . . The same is true with chalcopyrite although this latter mineral, like galena, is heavily coated in the absence of lime . . . . . On the other hand, when lime is added to a quartz-slime pulp, deposition on the sulphides is markedly enhanced . . . . . .

While lime is the reagent whose effects have been pictured, additional experiments have proved that it may be taken as typical of the other inorganic reagents that have been used in ordinary collective flotation. Sodium carbonate, sodium bicarbonate, sodium hydroxide, potassium tartrate, sulphuric acid, alum, barium chloride, etc.,

80 - Gates, J. F., and Jacobsen, L. K., Some Flotation Fundamentals and their Potential Application: Bull. of Univ. of Utah, vol. 16, No. 4, Aug., 1925, p. 38.

81 - Taggart, A. F., Taylor, T. C., and Ince, C. R., Experiments with Flotation Reagents: Am. Inst. Min. and Met. Eng., Tech. Pub. 204, Class B, Milling and Concentration, No. 17, New York, Mar. 1929, pp. 45-9

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have been found to have similar effects, differing with particular sulphide and gangue present.

. . . . . Addition to the Anaconda-slime pulp of cyanide and zinc sulphate (the bicarbonate was independently proved to be not effective alone) prevented any considerable slime deposition on galena . . . . . without materially changing that on the sphalerite . . . . . Pyrite also has a fairly heavy coating . . . . . in the presence of these reagents. Under relatively weak flotation conditions galena might be expected to float away from blende and pyrite in this pulp. Subsequent addition of more oil together with copper sulphate caused little change in the blende coating . . . . . although visual inspection indicates a slight reduction, but it does cause a marked increase in the coatings on galena . . . . . and pyrite . . . . Hence flotation conditions can be intensified sufficiently to float the blende without effecting any considerable raising of galena and pyrite.

The film formed by lime appears on the surface of the minerals somewhat like that obtained from a sulphide film formation, but the method of formation is of course different. Gates and Jacobsen[82] explain this as follows:

The effect of addition reagents such as lime and copper sulphate on the floative properties of galena, sphalerite, and pyrite, suggested the possibility of surface coatings or precipitates being deposited on the surfaces of the minerals. The reflecting microscope was freely used to determine the extent to which the surfaces of the different minerals had been affected by the treatment received, and proved to be of great aid in substantiating the existence of surface coatings. The coating produced by lime has a depressive effect on the three sulphides, and that produced by copper sulphate an accelerative effect on the flotation of sphalerite and pyrite. Photo-micrographs actually revealed superficial coatings deposited on the mineral surfaces. . . . . .

The existence of superficial coatings was clearly shown both by the microscope and by photo-micrographs; laboratory experiments indicate decided differences in the behavior of coated and uncoated minerals in the flotation cell. It remained to determine, if possible, the chemical nature and cause of these precipitates or coatings. Two typical cases were taken for this purpose, and were carefully studied. One was the coating present on galena after treatment in a circuit made alkaline by lime, and the other was that formed upon sphalerite in a circuit to which copper sulphate had been added.

In the lime circuit the amount of lime never exceeded three pounds per ton of ore, or a concentration of 0.037 per cent lime in the water. The maximum solubility of lime in water at room temperature is 0.13 per cent, the concentration, then, never exceeded the solubility of lime in water. If all the lime were in soluble form

82 - Gates, J. F., and Jacobsen, L. K., Page 51 of work cited.

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it is evident that, since there were no other reagents present, there must have been a reaction between the solute and other substance. A plausible explanation is that a reaction took place between the dissolved lime and the carbon dioxide content of the air beaten into the pulp during the agitation period.

$$CaO + H_2O = Ca(OH)_2 \qquad (1)$$

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O \qquad (2)$$

Calcium carbonate is practically insoluble in water that contains no carbon dioxide. It is probable that this insoluble precipitate, which is deposited on the galena and which so alters its behavior in the flotation cell, is calcium carbonate.

(B). Depression of Pyrite and Blende

Just how lime functions in flotation may be obscure, but the fact that it does function is well established. Lord and Snyder[83] discuss the use of lime as follows:

> . . . . . It may be used to neutralize acid salts present in ores or water. It is frequently an aid in clearing the froth of gangue for which purpose it may be best to add it in the cleaning operation. Lime is a strong depressant of pyrite and finds extensive employment for this purpose in the treatment of copper ores. Lime is used with zinc ores to retard pyrite, sometimes being added in the cleaner machines. Unless added in small amounts it depressed lead sulphide.

According to Weinig and Palmer:[84]

> Alkalis are used also as inhibiting or retarding agents, to prevent the flotation of some of the less easily floatable sulphide minerals, such as pyrite and sphalerite. The effect is due, presumably, to the formation of films of basic salts upon the mineral particles.

After stating that lime could be replaced by caustic soda and caustic potash, but because of its much lower cost and greater availability it is the most used alkaline reagent, Weinig and Palmer[85] continue in the same article:

> . . . . . Lime is extensively used by copper concentrating mills to prevent the flotation of pyrite . . . . .

Flotation reagents may be classified on various bases. Probably the most common and significant basis, however, is that of the apparent or supposed

83 - Lord, Robert, and Snyder, B. M., Notes on the Flotation Process: Bull. of Southwestern Eng. Corp., Los Angeles, Calif., June, 1929, p. 18.
84 - Weinig, A. J., and Palmer, I. A., Page 22 of work cited.
85 - Weinig, A. J., and Palmer, I. A., Page 22 of work cited.

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function in flotation, as frothers, collectors, depressants, etc. The classification is not "hard and fast" because a substance that one operator uses and classes as a frother may be used by another as a collector; still another may use it for the combined effect. According to Taggart[86] there are two essential phenomena in flotation.

(a) the degree of water-wetting of solid particles and

(b) the amount and character of froth.

The things that flotation agents do to affect and control these two fundamental phenomena may be grouped into five general classes; the groups of agents, named according to their functions, are; (1) Frothing agents; (2) Collecting Agents; (3) Depressing Agents; (4) Dispersion Agents; (5) Conserving Agents.

Lime plays a part in the last three groups as pointed out by Taggart:[87]

Dispersion agents are substances added to an ore pulp which effect the state of dispersion of the gangue particles and at the same time change the extent to which these particles adsorb at sulphide-particle surfaces . . . . . Common dispersion agents are sulphuric acid, lime, copper sulphate, soda ash, caustic soda, and sodium silicate . . . . .

Depressing agents is the name given to substances that are used to lessen the floatability of one or more of the minerals of the ordinarily-floatable class in a mixture of such minerals, e. g., to depress sphalerite when it occurs with galena, or pyrite when associated with chalcopyrite, and thus make it possible to float the galena and chalcopyrite respectively in concentrates relatively free of sphalerite or pyrite . . . . . .

The agents of this class do not all act in the same way. Most of them fall also in the dispersion-agent class; a few react chemically with some sulphides and not with others; and there is some evidence of a third type of action involving preferential deposition of a compound formed by the added agent and some constituent of the ore pulp other than the mineral upon which the salt deposits.

Depressing agents that are also dispersion agents include lime, sulphuric acid, sodium carbonate, sodium bicarbonate, sodium silicate, alkaline cyanide, zinc sulphate, copper sulphate, alum (potassium), and like inorganic substances. Their action is to effect differential adsorption of gangue at the sulphide surfaces.

Continuing, Taggart[88] says:

Conserving agents are substances added to ore pulps to protect the other flotation agents from attack by substances present in the

86 - Taggart, Arthur F., Pages 841, 844, and 845 of work cited.
87 - Taggart, Arthur F., Page 844 of work cited.
88 - Taggart, Arthur F., Page 846 of work cited.

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ore pulp. They are of no particular chemical character and may, in other pulps play some other part in the flotation operation. . . . . Lime used with ores containing free acid, when an alkaline xanthate is used as a collecting agent, is, in part at least, acting as a conserving agent.

Parsons[89] shows that lime was used early in selective flotation:

Lime - This reagent was one of the first to be used in flotation. It requires a time contact with the ore and, if possible, should be added in the grinding mills. It is used to overcome the deleterious effect of soluble salts which are frequently present in ores, but its principal use is as a depressant for iron sulphides in the selective separation of lead and zinc, copper and zinc, and copper and iron sulphides. It also has a marked depressing action on zinc sulphides in their separation from lead and copper. If added in too large amounts it will also prevent the lead from floating. Chalcopyrite will float in a strongly alkaline pulp, but chalcocite and some of the other copper minerals are affected by the least excess. Therefore, lime should not be used in their flotation. . . . . .

Farther on in his article Parsons[90] has the following to say regarding the use of lime in the flotation of ores containing lead, zinc, and iron sulphides:

In general, the selective separation of lead and zinc is obtained by the addition to the ore pulp of some reagent that will temporarily deaden the floating properties of the zinc, thus permitting the recovery of a high-grade lead concentrate. The separations are made more difficult by the presence of large amounts of iron sulphides, both pyrite and pyrrhotite, and then some reagent must be used which will permanently deaden these two sulphides so that they will not float with either the lead or zinc. The only reagents used which perform both these functions are sodium cyanide, sodium sulphite and sodium thiosulphate, but the following have been used with some success in temporarily deadening the zinc, zinc sulphate, sodium acid phosphate, and sodium hydrosulphite. The action of zinc sulphate is much more effective when used with sodium cyanide, the two being mixed. . . . . as they enter the flotation pulp. These reagents when used separately seem to have no effect in preventing the iron sulphides from floating.

These modifying reagents are used in an alkaline pulp, with either soda ash or lime. Lime has a permanent deadening effect on pyrite and pyrrhotite, and also affects galena in the same way but to a lesser degree . . . By the use of copper sulphate, the action of these modifying reagents is destroyed, and the flotative properties of the zinc minerals are revived . . . . . .

89 - Parsons, C. S., Selective Flotation: Eng. and Min. Jour., vol. 123, May 7, 1927, p. 758.

90 - Parsons, C. S., Page 759 of work cited.

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Weinig and Palmer[91] add the following concerning the use of lime in the lead-zinc separation:

> . . . . . If present in large quantities, lime practically inhibits the flotation of all sulphide minerals. For this reason lime is not used in lead-zinc separations where the mill water is used over again. The lime that is added to inhibit the flotation of pyrite in the zinc-iron separation would interfere with the flotation of galena in the head of the circuit. In such cases sodium carbonate is used to produce the alkalinity, because this reagent does not seriously hinder the flotation of the lead mineral . . . . . .

Robie[92] also writes of the use of lime in the lead-zinc circuit:

> Fresh water is used in the mill circuit, as the reagents used in floating the zinc make the water from the settling ponds unadaptable for lead flotation. Soda ash is used instead of lime, because it does not raise so much iron, and the pyrite is very readily floated when finely ground. Caustic soda gives too stiff and heavy a froth . . . . . .

Diamond[93] writing on the same subject says:

> Soda ash is used in the three mills as a conditioning and alkaline reagent. Caustic soda and lime have been found unsuitable in our operations, to date. The quantity of soda necessary for good work varies with the character of the ore being treated, our range being from 1 to 10 lbs. per ton. The demand is usually constant with each ore. Tailing solution can generally be returned for soda and heat saving, together with thickener overflows and filtrates, into the circuit without noticeable fouling.

Parsons[94] in writing about the separation of intimately mixed chalcopyrites, sphalerite, and iron sulphides says:

> This type of ore probably presents the most difficult of all selective flotation problems. The use of cyanide temperarily to deaden the zinc and permanently to deaden the iron sulphides seems essential. However, laboratory separations have been obtained by floating the copper in an alkaline pulp by the addition of lime. For the flotation of the zinc the copper tailing was dewatered to eliminate a part of the lime and the pulp then brought up to the required density by addition of fresh water. At this point soda ash was added and the zinc floated in a soda ash pulp, copper sulphate being used to help reactivate the zinc.

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91 - Weinig, A. J., and Palmer, I. A., The Trend of Flotation: Quart. Colorado Sch. of Mines, vol. 24, No. 4, 2d ed., Apr., 1928.
92 - Robie, Edward Hodges, Selective Lead Zinc Flotation at Sunnyside: Eng. and Min. Jour., vol. 121, May 8, 1926, p. 760.
93 - Diamond, R. W., Flotation Reagents at the Sullivan Mill: Min. and Met., vol. 8, Aug., 1927, p. 336.
94 - Parsons, C. S. Page 761 of work cited.

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In the following statement Johnson[95] disagrees with Parsons on the action of lime as a depressant for sphalerite:

> Mr. Parsons speaks of lime as an active depressant of sphalerite. On Chief ores this does not apply; lime actually increased the floatability of sphalerite if added in amounts up to 8 or 9 lbs. per ton of ore. In practice the addition of lime, as the hydrate, ranges from 2 to 4 lbs. per ton; additions in excess of 4 lbs. per ton tend to coagulate the gangue to such an extent that a high 'insoluble' content appears in the zinc concentrate. . . . . .

Booth[96] adds the following comment to this discussion:

> I believe that generally the use of lime has very little if any activating quality for the flotation of sphalerite. It is likely that when lime is used it sometimes give rise to the erroneous impression that sphalerite has been activated, whereas in reality the other minerals (pyrite in particular and possibly galena) have been depressed. I also find when using lime as a reagent in sphalerite flotation, especially large quantities of lime--and 8 or 9 lbs. per ton is a large quantity--that generally more copper sulphate is required for the actual activating than when using soda ash or other alkalies . . . . . .
>
> As regards the use of soda ash, I have tested a number of ores in which pyrite flotation was improved by its use. Usually, however, its benefits are more apparent than real. It usually gives a better looking pyrite mineral froth, and occasionally the assays show a better recovery of iron.
>
> In the testing of ores containing large quantities of pyrrhotite, I have found that copper sulphate has a decided activating effect on the pyrrhotite, especially if some means are not taken for depressing the mineral previous to the addition of the copper sulphate.

Another record of the use of lime in flotation is given by MacDonald[97]:

> Selective flotation, in this sense, between chalcopyrite and pyrite, has been achieved in the mill of the Moctezuma Copper Co. at Nacozari, Sonora, Mexico, to the extent that over 90 per cent of the iron combined as pyrite in the original mill feed is now being rejected, whereas the percentage of copper recovered remains almost at the high level obtained when but 25 per cent of the pyrite iron was being rejected . . . . . .
>
> Dry lime is fed mechanically onto the ore conveyors leading from the fine-ore bins to the primary mills . . . . . .

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95 - Johnson, Homar L., The Action of Certain Reagents in Selective Flotation: Eng. and Min. Jour., vol. 123, June 4, 1927, p. 931.
96 - Booth, Lionel E., Effects of Bichromate in Flotation at the Sullivan Mill: Eng. and Min. Jour., vol. 124, July 23, 1927, p. 141.
97 - MacDonald, Wm. T., Pages 445-454 of work cited.

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Best flotation results are obtained when the tailing pulp shows a lime content equivalent to 0.15 to 0.35 lbs. of calcium oxide per ton of clear solution, depending somewhat upon the quality of the lime used. When the alkalinity falls below this minimum, high flotation tailing usually ensues, whereas an unduly high alkalinity changes the character of the froth unfavorably and involves a waste of reagent.

When a good quality of lime is available, the consumption averages from 5 to 6 lbs. per ton of flotation feed . . . .

The functions of lime in flotation include the neutralizing of natural acids, precipitation of possibly detrimental soluble salts, prevention of oxidation of the sulphides, coagulation and defloccula-tion, and modification of physical properties of the electrolyte.

Locke[98] writes of the separation of lead, copper, and iron as follows:

One section of the new Utah Apex mill handles lead-copper-iron sulphides. The lead and copper are first floated together by the use of xanthate, thus eliminating the iron with the tailings. The lead-copper froth is next conditioned with 1 lb. lime and 0.5 lb. sodium sulphide per ton, thus deadening the copper and enabling the lead to be floated from it in the final separation step.

Geiser[99] mentions the use of lime in differential flotation and also the questionable advantage of lime in a lead-zinc circuit:

Lime is the most important alkaline reagent employed in flotation today; it is generally cheap and abundant and as its positive action in depressing pyrite is becoming better understood, more plants are adopting it. The rejection of barren pyrite in the concentration of copper ores by the use of lime and the T-T mixture or xanthate has made profitable the treatment of lower grade ores and has enabled mines to keep operating which would otherwise be forced to discontinue during the present low price of copper. It is generally used on copper ores, but frequently excellent results can be obtained on lead-zinc ores. The amount to use will vary in individual cases, but is generally critical, probably not over one pound per ton of solution being sufficient. . . . . , High alkalinity will depress galena, but has not so harmful an effect on the sphalerite, though more xanthate will be needed . . . . .

In the selective flotation of chalcopyrite and nickel minerals in the presence of pyrrhotite the essential requirements are the same as in eliminating pyrite--namely, pulp made alkaline by lime or soda ash, and the new flotation agents. The chalcopyrite floats with more ease than the nickel minerals.

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98 - Locke, Chas. E., Flotation Dominates Ore-Dressing Progress: Eng. and Min. Jour., vol. 123, Jan. 22, 1927, p. 151.

99 - Geiser, H. S., Flotation Reagents and Practice: Eng. and Min. Jour., vol. 123, May 21, 1927, pp. 843-44.

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(c). Depression of Gold and Copper Metallics

In connection with the flotation of metallic copper Fahrenwald[100] says that proper alkalinity control is important and that lime may be used, although he advocates sodium dibasic phosphate:

> . . . . . On some samples, tailings carrying as little as 0.06 per cent copper were repeatedly obtained.
>
> Xanthate in a slightly alkaline pulp in conjunction with a variety of oils was the reagent combination used. Lime or sodium carbonate or sodium dibasic phosphate in small quantities gave satisfactory alkalinity. Sodium dibasic phosphate was the best of these substances; a given quantity was satisfactory, regardless of the mill from which the table-feed samples were taken. Lime or soda ash called for closer regulation. The mill water was slightly less than pH = 7 and a pH of 7.5 to 8 was required . . . .

Regarding gold and silver ores von Bernewitz[101] says in conclusion:

> . . . . . More interest is being taken in the flotation of gold--and silver--bearing ores, and the scope of the process is widening.

Substantiating this statement is a current press report[102] which shows how flotation is competing with cyanidation:

> McIntyre Porcupine Mines, second largest gold producer in the Porcupine district of Ontario, will build a 2000-ton flotation plant to replace the present 1500-ton cyanidation mill . . . . .

The importance of lime in this new flotation is brought out by Parsons[103] in discussing differential flotation of complex ores with and without gold:

> Successful separation of chalcopyrite from the iron sulphides, both pyrrhotite and pyrite requires the solution of two problems. The first problem is to free the copper mineral from the iron . . . . The second problem is to prevent the iron from floating with the copper. With chalcopyrite ore containing no gold this can generally be done by maintaining a pulp strongly alkaline with lime. Lime has a permanent deadening effect on pyrite and pyrrhotite and very high ratios of concentration can be obtained.
>
> As a general rule, copper ores containing gold present an entirely different problem, that of recovering the gold in the copper

100 - Fahrenwald, A. W., Xanthate and Pure Oil Float Native Copper in Amygdaloid Ores: Eng. and Min. Jour., vol. 126, July 14, 1928, p. 59.
101 - von Bernewitz, M. W., Flotation in the Treatment of Gold and Silver Ores; A Review: Eng. and Min. Jour., vol. 124, Oct. 15, 1927, p. 657.
102 - Engineering and Mining Journal, vol. 129, June 23, 1930, p. 631.
103 - Parsons, C. S. Page 760 of work cited.

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concentrate. The use of lime to retard the iron, except in rare instances, tends to throw the greater part of the gold with the iron tailing. Soda ash or caustic soda is used because it has not the detrimental effect on gold, but unfortunately it does not deaden the pyrite. Its effect is sufficient to keep the pyrrhotite from floating, but pyrite floats readily. Soda disperses or deflocculates gangue slime, whereas lime coagulates it. However, soda also seems to tend to coagulate the sulphides.

Sodium cyanide added to a pulp, the alkalinity of which is maintained with soda ash, can be used permanently to deaden at least a part of the pyrite, but it also often has a modifying effect on the chalcopyrite. The chalcopyrite can be reactivated by the addition of a limited amount of copper sulphate. By the use of cyanide under these conditions it is often possible to obtain a higher ratio of concentration without lowering the recovery of gold.

In connection with what Parsons says concerning the gold in flotation, Thomas, Christmann, and Gifford[104] write:

> The third example is an ore from Southwestern United States assaying 1.87% copper and 14.8% iron. The ore contains some metallic copper and the comparison of lime and cyanide is of special interest for this reason. It has been observed on several occasions that lime is a powerful depressant for metallics, whether gold or copper, and this is well brought out by the data . . . . . where the lowering of the recovery caused by the use of lime is doubtless attributable, in part at least, to failure to recover metallic copper . . . . . .

To this, von Bernewitz[105] cites a case where: "Flotation in a high-alkaline cyanide solution was not a success . . . . . .

CONCLUSION

Thus, lime, which was one of the first chemicals to be used by man, is still one of the most important industrial reagents. Its use as a purifier in the treatment of water has been well established; and in milling it has served for many years in cyanidation and amalgamation. In the last five years it has become the most generally used flotation reagent. About 2.5 per cent of the nation's output is consumed by the flotation process alone.

Since there are many varieties of lime and each has its advantages and disadvantages, the operator who has occasion to use it is confronted with the question of a choice. Such a choice must be guided by both technical and economic considerations. Consequently, no general recommendation is warranted, for what is good practice at one mill may be questionable elsewhere.

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104 - Thomas, Christmann, and Gifford, Page 6 of work cited.
105 - von Bernewitz, M. W., Page 657 of work cited.

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Limes vary greatly in composition and properties; but the multiplicity of its uses gives a field of application for practically every variety. On the other hand, the types suitable for a particular operation may be very limited. There may be one variety which is superior, but a less desirable lime may be chosen because of its cheapness. An economic balance between advantages and disadvantages must be established, and that must be by the operator.

In general, for flotation, a high-calcium hydrated lime is probably the most favored. It is active as a neutralizer of acid, imparts alkalinity, is a purifier and a depressor, and is easily handled. Its chief disadvantage is its cost. Economically, leaner limes might be justified despite their inefficiency.

The chemical, lime (CaO), is the most desirable constituent of a "lime," and hence the "available lime" content is often an indication of the value of the material. Quicklime is CaO (plus impurities) and therefore might be considered better than the hydrate (CaOH) or those limes which contain magnesia (MgO) and other impurities. However, the hydrate is easier and safer to handle, and in some cases dolomitic limes are not disadvantageous. For neutralizing acid, dolomitic lime is very effective, but it is not efficient in imparting alkalinity because the magnesium hydrate is insoluble. If free acid is to be neutralized, unburned limestone may be used, and subsequent treatment may be done with lime. Most of the impurities in lime act only as fillers and are not harmful in themselves; the chief active constituent is the soluble calcium oxide or hydroxide.

In choosing a lime, an operator must consider the purpose of adding lime, the properties of the particular lime chosen, and the value of the limes with respect to their costs. Since there are no hard and fast rules to govern the selection, operators differ in opinion and final choice of lime.

The method of using lime is also subject to personal opinion and plant operation. In general, lime for water purification and as a reagent in flotation should be added to the circuit early enough to allow it to be most effective in its reactions.

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